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THE ELECTRON IN CHEMISTRY

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BEING FIVE LECTURES DELIVERED AT
THE FRANKLIN INSTITUTE,
PHILADELPHIA

BY

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PREFACE

This book contains the substance of five lectures delivered at The Franklin Institute, Philadelphia, in April, 1923. My warmest thanks are due to the Members of the Institute whose admirable arrangements and boundless hospitality made the delivery of these lectures one of the most delightful episodes in my life. The choice of chemistry as a subject for lectures by one whose work has been mainly in physics seems to call for some explanation.

It has been customary to divide the study of the properties of matter into two sciences, physics and chemistry. In the past the distinction was a real one owing to our ignorance of the structures of the atom and the molecule. The region inside the atom or molecule was an unknown territory in the older physics, which had no explanation to offer as to why the properties of an atom of one element differed from those of another element. As chemistry is concerned mainly with these differences there was a very real division between the two sciences.

In the course of the last quarter of a century, however, the physicists have penetrated into this territory and have arrived at conceptions of the atom and molecule which indicate the way in which one kind of atom differs from another and how one atom unites with others to form molecules. These are just the problems which are dealt with by the chemists and thus if the modern conception of the atom is correct the barrier which separated physics from chemistry has been removed.

From many points of view the chemical side seems to be the one on which the most striking developments of the newer physics may be expected. In the first place the problems are of the greatest intrinsic importance and, secondly, in the vast mass of information accumulated by chemists with regard to the combination of atoms we have unrivalled means of testing the truth of any conclusion to which the theory may lead us.

In the newer physics the atom is regarded as made up of a number of electrons arranged round a central charge of positive electricity. The number and arrangement of the electrons determine the properties of the atom and the action of one atom on

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another. The electron is the dominating factor in these problems which are just those with which the chemist is most concerned and hence it would seem that the electron must be the dominating factor in chemical theory and that it is important to interpret chemical problems in terms of electrons and their arrangements. The object of these lectures was to make an attempt to do this. I have in them limited myself to the consideration of the chemical aspects of the electron theory of the atom and have followed a theory of the relation of the electron to chemistry at which I have been working for many years and which has been the subject of numerous lectures at the Royal Institution, London, and of several papers in the *Philosophical Magazine.*

J. J. THOMSON.

TRINITY LODGE,
CAMBRIDGE, June, 1923.

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THE ELECTRON IN CHEMISTRY

CHAPTER I.

I OUGHT to explain why it is that I, who am a physicist and not a chemist, have chosen chemistry as the subject of these lectures. I have done so because I believe that the introduction of the idea of the electron will break down, and indeed has already done so to some extent, the barrier of ignorance which has divided the study of the properties of matter into two distinct sciences, physics and chemistry. The properties of matter which are of primary importance to the chemist are those which relate to the power of atoms to unite together to form new combinations, new compounds. The ability to do this and the type of compound formed vary enormously from one chemical element to another. Until recently the conception formed by the physicist of the atom afforded no clue to this variation in the chemical properties of the atom and gave therefore but little guidance to the chemist in what he regarded, and quite rightly, as the most important part of his work. The chemist wants to know much more about the difference between an atom of hydrogen and one of oxygen than that the atom of hydrogen is a small particle of one kind of matter and the atom of oxygen a heavier particle of another kind of matter. This lack of knowledge led to a proposal made by a distinguished chemist at the beginning of this century to give up the atomic theory and base chemistry on statistical and thermodynamical considerations.

The chemist wants to know the reason why the behaviour of an atom of hydrogen is so different from that of one of oxygen. This must depend upon the differences in the constitution of the two atoms themselves. Thus to explain the difference between the chemical properties of different atoms we have to go a stage further than the atomic theory. Just as some of the physical properties of matter in bulk had required for their explanation the conception that matter is not continuous but has a structure of finite and measurable fineness, so no progress could be made towards the explanation of their chemical properties until we gave up the idea that the atom was indivisible, continuous and uniform, and assigned to atoms as well as to solids and liquids a structure of their own. The discovery of the electron in 1897 was the first direct evidence of such a structure. It was shown that these electrons came from all types of atoms, and that whatever the source there was only one kind of electron, which has a mass only about 1/1700 that of an atom of hydrogen and carries a charge of negative electricity numerically equal to the positive charge associated with an atom of hydrogen in the electrolysis of solutions.

Thus an invariable electron was proved to be a constituent of all atoms. Means were then devised to measure the number of electrons in the atoms of the different chemical elements. It was found that this number was finite and varied from element to element, and that the number of electrons in the atom of an element was equal to the atomic number of the element: the atomic number of an element being its place in the list when the elements are arranged in the order of their atomic weights. As the atomic number is roughly proportional to the atomic weight the proportion between the mass of the electrons and the total mass of an atom is, except for hydrogen, much the same for all atoms. The electrons, however, only account for about 1/3400 of the whole mass, for most purposes a negligible fraction.

The greater part of the mass is accounted for by the positively electrified part of the atom. The electrons are all negatively electrified and as the normal atom is electrically neutral, there must be within it a positive charge to balance the negative one on the electrons. This positive charge, as experiments on positive rays show, is attached to a mass equal to the mass of the atom. Thus the carrier of the positive charge, unlike that of the negative, varies from element to element. As the mass of the positive charge is always an integral multiple of a unit, it is natural to suppose that this mass is made up of a number of units bound together. The number of such units is equal to the atomic weight and the number of electrons approximately half that number, if each unit of mass carries the atomic charge of positive electricity, the quantity of positive electricity would be too large unless these positive units were associated with about half their number of electrons. Thus, in addition to the structure conferred by the electrons, the positively electrified parts have themselves a structure, it is the structure conferred by the electrons which is responsible for the chemical properties of the atom, the structure of the positive core is concerned with radioactive transformations.

As up to the present nothing has been discovered that cannot be resolved into electrons and positively electrified particles, it is natural to frame a theory of the structure of the atom on the supposition that it is built up of these two ingredients. It should be borne in mind, however, that our means of detecting the existence of electrically charged bodies far surpass those for detecting uncharged ones, and if there were any uncharged constituents of the atom, they would in any case probably have escaped detection. We know, however, that even supposing such constituents do exist, their mass must be negligible compared with that of the positive parts, for these parts account for well within a fraction of a per cent. of the whole mass of the atom.

ARRANGEMENT OF ELECTRONS IN THE ATOM.

Confining ourselves then to the consideration of things whose existence has been demonstrated we regard the atom as made up of a massive positively electrified centre surrounded by electrons. The number of electrons increasing from one in the atom of hydrogen to a hundred or more in the heavier elements. The positive charge of the centre and the negative charges on the electrons will produce a field of electrical force which will be determinable when the position of the electrons can be specified. Thus the force exerted by the atom and therefore its chemical properties will depend upon the configuration of the electrons and to determine this is one of the most important problems in the electron theory of chemistry.

This problem is that of determining the way the electrons will arrange themselves under the action of their mutual repulsions and the forces exerted upon them by the positive charge.

In the first place we observe that if these forces were to vary strictly as the inverse square of the distance we know by Earnshaw's theorem that no stable configuration in which the electrons are at rest or oscillating about positions of equilibrium is possible, the electrons must describe orbits, and further they must describe different orbits; for such a system as that in Saturn's rings where several units follow each other round the same orbit is not possible when the units, as the electrons would do, repel each other instead of attracting one another like the constituents of Saturn's rings. When there are several electrons in the atom the orbits described by the electrons would be of great complexity, and the mental picture conveyed by this multitude of orbits would be too blurred and complicated to be of much assistance in helping us to get readily a clear idea of what is going on in chemical processes.

I have therefore adopted the plan of supposing that the law of force between the positive part and the electrons is, at the distances with which we have to deal in the atom, not strictly that of the inverse square, but a more complex one which changes from attraction to repulsion as the distance between the positive charge and the electron diminishes. This hypothesis leads to a simple mental picture of the structure of the atom and its consequences are in close agreement with the facts of chemistry. I suppose that the repulsive force between two *electrons* is always inversely proportional to the square of the distance. With regard to this point I may point out that we have no direct evidence as to what may be the law of force between electrical charges at distances comparable to 10^{-8} cm., which is a distance which we have reason to believe is comparable with that which separates the positive charge from the electron in the atom. The direct experimental verification of this law has been of course made at incomparably greater distances, while the direct experiments, such as those on the scattering of the alpha particles, only give information as to the law at distances very small compared with 10^{-8} cm.

I shall assume that the law of force between a positive charge and an electron is expressed by the equation

$$F = \frac{Ee}{r^2}\left(1 - \frac{c}{r}\right) \tag{1}$$

where F is the attraction between the charges, E, e, the positive and negative charges on the core and electrons, respectively, r the distance between them and c is a constant varying from one kind of atom to another, it is the distance at which the force changes from attraction to repulsion and is of the order of 10^{-8} cm.

We may remark in passing that the introduction of some new physical law, involving directly or indirectly a length of this order, is necessary for any theory of the structure of atoms. We could not form a theory at all if all we knew about the action of electric charges was that they repelled or attracted inversely as the square of the distance, for this would put at our disposal only two quantities, the mass of an electron and its charge, and so could not furnish the three units of space, mass and time required for any physical theory. The discovery of the induction of currents or what is equivalent, the magnetic effect due to electric charges, introduced another fundamental unit the velocity of light; the unit of length to which this system leads is the radius of the electron, about 10^{-13} cm., a quantity of quite different order from 10^{-8} cm., which corresponds to atomic dimensions. The size of atoms being what it is, is a proof that there is some law of physics not recognized in the older science which is all-important in connection with the theory of the atom and must form the basis of that theory.

If the law of force is that just given, then a number of electrons can be in stable equilibrium around a positive charge without necessarily describing orbits around it.

ONE ELECTRON ATOM.

Thus, for example, if there is one electron it will be in stable equilibrium at a distance c_1 from the positive charge.

TWO ELECTRON ATOM.

If there are two electrons they will be in equilibrium with the positive charge midway between them, r the distance of either electron from the positive charge is given by the equation

$$\frac{Ee}{r^2}\left(1-\frac{c_2}{r}\right)=\frac{e^2}{4r^2} \qquad (2)$$

When the positive charge and the two electrons form an electrically neutral system $E = 2e$, so that $c_2/r = 7/8$ or $r = 1.14\, c_2$.

THREE ELECTRON ATOM.

When there are three electrons, they will be in equilibrium at the corners of an equilateral triangle with the positive charge at the centre. r, the distance of any electron from the centre, is given by the equation

$$\frac{Ee}{r^2}\left(1 - \frac{c_3}{r}\right) = \frac{2e^2}{3r^2}\cos 30 \quad . \quad . \quad . \qquad (3)$$

When the system is electrically neutral $E = 3e$, so that $r = 1.24\, c_3$.

FOUR ELECTRON ATOM.

The most symmetrical arrangement of four electrons is when they are at the corners of a regular tetrahedron. The distance of the electrons from the centre when the atom is neutral is equal to $1.29\, c_4$. The tetrahedron may be regarded as the ends of two equal lines at right angles to each other and also to the line joining their middle points.

FIVE ELECTRON ATOM.

Five electrons are in equilibrium when arranged so that three are at the corners of an equilateral triangle, the other two at the ends of a line passing through the centre of the triangle and at right angles to its plane; the line is bisected by the plane of the triangle. The distance of the electrons in the triangle from the centre is $1.34\, c_5$, that of the other two $1.37\, c_5$.

SIX ELECTRON ATOM.

Six electrons are in equilibrium when at the corners of a regular octahedron. For some purposes it is convenient to regard the octahedron as two equilateral triangles at right angles to the line joining their centres, one triangle being twisted relatively to the other so that the projection of their corners on a parallel plane forms a regular hexagon. The distance of the electrons from the centre is $1.38\, c_6$.

SEVEN ELECTRON ATOM.

Seven electrons arrange themselves so that five are at the corners of a regular pentagon while the two others are at the ends of a line through the centre at right angles to the plane of the pentagon and which is bisected by that plane. The distance of the electrons in the pentagon from the centre is $1.4\, c_7$, that of the other two $1.37\, c_7$.

EIGHT ELECTRON ATOM.

Eight electrons arrange themselves at the corners of a twisted cube, a figure obtained by taking two squares, placing them parallel to each other and at right angles to the line joining their centres, and twisting them relatively to each other so that the projection of their corners on a parallel plane forms a regular octagon.

CONFIGURATION WHEN THE NUMBER OF ELECTRONS IS GREATER THAN EIGHT.

The following considerations show, however, that there must come a stage when it will no longer be possible to have all the electrons at the corners of a regular polyhedron.

To keep the electrons in stable equilibrium in spite of their mutual repulsion requires a finite positive charge and the greater the number of electrons and therefore the smaller the angular distance between an electron and its nearest neighbour, the greater the positive charge must be.

In Table I, I give the results of a calculation of the positive charge E required to keep n electrons in stable equilibrium. The first line refers to the two-dimensional problem, when the electrons are arranged at equal intervals round the circumference of a circle with a positive charge at the centre; the second line refers to the three-dimensional problem when the electrons are at the corners of a polyhedron.

These numbers are for a law of force between the positive charge and the electron represented by $\frac{Ee}{r^2}\left(1-\frac{c}{r}\right)$. If the part of the force which does not vary inversely as the square of the distance varies inversely as some higher power than the cube, then the number of electrons which a given positive charge can keep in stable equilibrium will be increased.

TABLE I.

Two-dimensional problem.

$n = 1$	2	3	4	5	6	7	10	12	14	16	8
$E/e > 0$	.75	1.58	3.10	4.76	7.32	14.2	24.48	38.9	58	83	115

Three-dimensional problem.

$n = 1$	2	3	4	6	8	12	20
$E/e > 0$	.75	1.58	2.44	4.8	7.6	13	30

Confining ourselves for the moment to the case when the force is represented by $F = \frac{Ee}{r^2}\left(1-\frac{c}{r}\right)$, we see from the second table that when the number of electrons is not greater than eight, the electrons can be kept in equilibrium by a positive charge equal to the sum of the negative charges on the electrons, which is the greatest positive charge which can occur in a neutral atom. So that when the number of electrons is not greater than eight, a neutral atom can have these electrons arranged symmetrically at the same distance from the centre at the corners of a regular polyhedron. When, however, the number exceeds eight this is no longer possible. For we see from the table that to keep, say, nine electrons in stable equilibrium would require a positive charge more than $9e$, where e is the charge on an electron, but in a neutral molecule $9e$ is the maximum positive charge available when there are nine electrons in the atom. Thus the regular progression in the arrangement breaks down when the electrons amount to eight and a new arrangement must come into force. Let us suppose that there are nine electrons; then these nine cannot all be arranged at the same distance from the centre, for this arrangement would be unstable since a positive charge of nine is insufficient to keep nine electrons in stable equilibrium. The charge $9e$ could, however, keep eight electrons in stable equilibrium at the same distance from the centre, leaving one to go outside. The distance of the eight electrons from the central charge would be $1.38\ c_9$, that of the single electron would be $9\ c_9$. So that the single electron would be a long way out from the centre of the atom.

If there are ten electrons, these can be arranged so that eight form a layer round the centre and two go outside, the distance of the eight from the centre would be $1.33\ c_{10}$, that of the two outlying ones would be $5.7\ c_{10}$.

Eleven electrons can be arranged with an inner layer of eight and an outer one of three, the distance of the inner one from the centre would be $1.3\ c_{11}$, that of the outer one $4.625\ c_{11}$.

Twelve electrons might be arranged with an inner layer of eight, radius $1.26\ c_{12}$ and an outer layer of four, radius $3.9\ c_{12}$.

Thirteen electrons, with an inner layer of eight, radius $1.227\ c_{13}$ and an outer layer of five, mean radius $3.52\ c_{13}$.

Fourteen electrons, with an inner layer of eight, radius $1.22\ c_{14}$; and an outer layer of six, radius $3.22\ c_{14}$.

Fifteen electrons, with an inner layer of eight, radius $1.2\ c_{15}$; and an outer layer of seven, mean radius $3.1\ c_{15}$.

Sixteen electrons, with an inner layer of eight, radius 1.18 c_{16}; and an outer layer of eight, radius 2.9 c_{16}.

We have now got eight electrons on the outer layer and there is not accommodation for any more; for since the atom is neutral the excess of positive over negative electricity in the system consisting of the central charge and the inner layer is equal to the charge on the electrons in the outer layer, thus if there were nine electrons in the outer layer there would be only an effective positive charge of nine to keep them in equilibrium. We can, however, get a system which will be in stable equilibrium if the electrons proceed to form a third shell; thus, if there are seventeen electrons, we could have an inner shell of eight, then another shell of eight and then an electron a long way outside. If we had eighteen electrons we should get two shells of eight and two electrons outside, and so on, until with twenty-four electrons we shall have filled up the third shell and have to begin again.

Let us now arrange the lighter elements in the order of the number of electrons they contain, and place underneath the symbol for the element the number of electrons in the outer layer of the atom. The number of free electrons in the atom has been taken as two less than the atomic number of the element, since two electrons always seem to cluster round the centre core and form a system by themselves.

TABLE II.

	Li	Be	Bo	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	A	K
Number of free electrons in the atom . .	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Number of electrons in the outer layer .	1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8	1

THE PERIODIC LAW.

Thus, if we arrange the elements in the order of the number of electrons in the atom, which we have seen is the same as the order of the atomic weights, there will be a periodicity in the number of electrons in the outer layer. It will increase from one to eight, then drop again to one; increase again to eight, drop to one, and so on. Thus, as far as properties depending upon the outer layer are concerned, the elements will show a periodicity in their properties similar to that expressed by Mendeleef's periodic law in chemistry.

We shall show later on that the valency is a property depending on the number of electrons in the outer layer, the electropositive valency being proportional to that number, so that this type of atom would explain the periodic law.

VARIATION OF THE NUMBER OF ELEMENTS IN A PERIOD.

We have supposed that when the positive charge and therefore the number of electrons in the atom is increased by unity, the additional electron goes to the outer layer. This need not, however, necessarily be the case. When the positive charge is increased, the number of electrons which it can hold in stable equilibrium on a spherical layer with its centre at the atom increases also; thus a large positive charge at the centre could hold more than eight electrons in the inner layer, and so the additional electron might, instead of going to the outside, find accommodation on one of the inner layers. Thus, since the valency depends on the number of electrons in the outer layer, if the additional electron was trapped in an inner layer, two consecutive elements, though they would have different atomic weights, would have the same valency. When there are a large number of electrons in the atom arranged in many layers it may require the addition of several electrons to the atom before there is any increase in the number in the outer layer and thus there might be a considerable number of adjacent elements with different atomic weights but with very similar chemical properties. There are groups of elements such as the iron, nickel and cobalt group, the rhodium group, the crowd of elements known as the rare earths, and the platinum group which fulfil this condition.

ALLOTROPIC FORMS.

There is in general more than one way in which the electrons can be arranged in stable equilibrium and though one particular arrangement may have the absolute minimum potential energy, yet calculation shows that in some cases the difference in potential energy between this configuration and some other one is exceedingly small and changes in the surroundings may change the balance in favour of one or the other. If these configurations have different numbers of electrons in the outer layer, then they will correspond to forms with different valencies, and thus we may look in this direction for an explanation of the variable valencies shown by some elements. We shall return to this point later on.

The table, next page, calculated by Miss Woodward, gives in the third column the potential energy corresponding to the various arrangements of the electrons in atoms containing from three to eight electrons. The second column contains the distances of the electrons from the centre of the atom. Thus the figures corresponding to the arrangement of seven electrons in a double triangular pyramid with two electrons outside on the axis of the pyramid, indicate that the electrons on the triangular base are at a distance 1.244 c from the centre; those at a vertex of the inner pyramid at the distance 1.191 c while the outer electrons are at a distance 4.316 c.

A simple example of the small difference in the potential energy between different configurations is afforded by an atom containing five electrons. We have described one such configuration when the five electrons were approximately at the same distance from the centre. There is, however, as we see from the table, another arrangement where four electrons are at the corners of a regular tetrahedron with its centre at the positive charge, while the fifth electron is a long way outside the tetrahedron. The mean distance of the electrons on the tetrahedron from the centre is approximately 1.22 c_5; where c_5 is the value of c for the fifth electron atom, while that of the outside electron is approximately 5 c_5, *i.e.,* more than four times greater. The potential energy of the second configuration is only about two per cent. greater than the first, thus there would be no great tendency for the second configuration to pass back to the other. The properties of the two configurations would, however, be quite different, in the second configuration we have a single electron far away from the others, this, as we have seen, is also the case with the alkali metals, in this configuration the five electron atom might be expected to show some of the properties of a monovalent element, in the other it would be pentavalent.

ACTIVE NITROGEN.

As nitrogen has an atom with five disposable electrons, it seems possible that the active form of nitrogen discovered by the

TABLE III.

Potential Energy of Atoms with Three to Eight Electrons.

Arrangement of Electrons.	Distances of Electrons from Atom.	Potential Energy.
Eight electrons.		
(i) One layer—twisted cube	$1.447c$	$-16.75\ e^2/c$
(ii) One layer—cube	$1.446c$	$-15.28\ e^2/c$
(iii) Two layers—tetrahedra similarly orientated	$1.105c$ (4) $3.108c$ (4)	$-14.77\ e^2/c$
(iv) Two layers—six electrons in inner, two in outer ring	$1.282c$ (4) $1.267c$ (2) $4.80\ c$ (2)	$-15.012\ e^2/c$
Seven electrons.		
(i) One layer	$1.37\ c$ (2) $1.439c$ (5)	$-12.181\ e^2/c$
(ii) Two layers—five in inner, two in outer ring	$1.244c$ (3) $1.191c$ (2) $4.316c$ (2)	$-12.096\ e^2/c$
Six electrons.		
(i) One layer	$1.385c$	$-9.40\ e^2/c$
(ii) Two layers—four in inner, two in outer ring	$1.196c$ (4) $3.55\ c$ (2)	$-8.868\ e^2/c$
Five electrons.		
(i) One layer	$1.342c$ (3) $1.376c$ (2)	$-6.806\ e^2/c$
(ii) Two layers—four in inner, one in outer ring	$1.273c$ (3) $1.134c$ (1) $5.105c$ (1)	$-6.667\ e^2/c$
Four electrons.		
(i) One layer—corners of square	$1.298c$	$-4.748\ e^2/c$
Three electrons.		
(i) One layer—equilateral triangle	$1.238c$	$-2.934\ e^2/c$
(ii) Electrons on a straight line through atom	$1.087c$ $1.035c$ $3.577c$	$-2.787\ e^2/c$

present Lord Rayleigh may have this configuration. This active form is produced by passing an electric discharge through nitrogen and it is clear that if an atom were first ionised by the detachment of an electron the conditions would be favourable for the production of the configuration under consideration. For when the first electron is detached the remaining four will naturally arrange themselves in a tetrahedron round the centre, thus the nucleus of the configuration is already there and an additional electron at some distance from the centre would be more likely to take up a position outside than to force itself into the tetrahedron. As the second form has, like the alkali metals, a single electron at a great distance from the centre, we should expect that like them it would be attacked vigorously by halogens, and that as the outlying electron would require little work to detach it, this form of nitrogen would be easily ionised; both these properties are characteristic of Lord Rayleigh's active nitrogen.

We see that besides the two forms for the five electron atom there are forms both for the six and seven electron atoms (*e.g.*, oxygen and fluorine) which differ little in their potential energy in which two electrons are separated from the rest. These would tend to be formed if the atoms were ionised so as to lose two electrons and then regained these electrons. As the number of atoms which lose two electrons when the electric discharge passes through a gas is small compared with the number which only lose one, we should not expect these modifications of oxygen and fluorine to be produced so freely as that of nitrogen.

EXPERIMENTAL EVIDENCE AS TO THE CONFIGURATION OF ELECTRONS IN THE ATOM.

We may hope when our sources of Röntgen radiation are more powerful to be able to obtain evidence of this by observing the interference effects produced when Röntgen rays pass through large numbers of neutral atoms. If the orientation of these atoms is a random one we can easily show that the interference of the rays scattered by the electrons will give rise to a series of rings. There will be a separate ring for every different distance between pairs of electrons in the atom. Thus if there were only two electrons there would only be one ring whose radius is proportional to the distance between the two electrons; again in an equilateral triangle there would only be one ring, for the distance between any two electrons is equal to a side of the triangle. If four electrons were at the corners of a regular tetrahedron there would again be only one ring for the distance between any two electrons is equal to a side of the tetrahedron. If, however, the four electrons were at the corners of a square there would be two rings, the radius of one being proportional to a side of the square, that of the other to its diagonal. Arrangement at the corners of a regular octahedron would also give two rings, the radius of one being proportional to the side of the octahedron, the other to the distance between two opposite corners. A cubical arrangement of electrons would, however, give three rings, the radius of one proportional to a side of the cube, that of the second to a diagonal of a face and that of the third to the diagonal of the cube. Evidence of this kind is not, however, available at present.

As we shall see later on, the coefficient of diamagnetism gives on Langevin's theory of diamagnetism, the moment of inertia of the electrons about a line through the centre of the atom, this can be made to yield a certain amount of information about the disposition of the electrons, especially if we know from other sources the distance of the outer layer of electrons from the centre of the atom.

EVIDENCE AFFORDED BY POSITIVE RAYS

More definite information can be got from evidence afforded by the positive rays. Let us first take the case of positively charged atoms. Their positive charge is due to their having lost electrons from the outer layer, now on this theory there is only one electron in the outer layer of the atom of hydrogen and in those of the alkali metals, so that these atoms should not be able to lose more than one electron and therefore should be unable to gain more than one unit of positive charge.

It is remarkable that these are the only atoms which in the positive ray spectra have not been observed with more than one positive charge. On the other hand, other light atoms have more than one electron and thus gain double or treble positive charges.

All such atoms when detected in the positive ray spectrum have been observed with double positive charges and in some cases such as carbon, nitrogen, oxygen with three or four, while as many as seven positive charges have been found in the atom of mercury.

Further confirmation of the views we have been discussing about the relation between the number of electrons and the property of the atom is afforded by the study of the occurrence of negatively electrified atoms in a gas through which an electric discharge is passing. By the method of the positive rays we are able to detect negatively as well as positively electrified atoms, and we find in this way that some atoms readily acquire a negative charge while others never do so. On the view we are considering, eight is the maximum number of electrons which can exist in the outer layer; as the atom of neon already possesses this number it cannot accommodate another electron and so cannot receive a negative charge. On the other hand the atom with a smaller number of electrons in the outer layer has, as a reference to Table II shows, a superfluity of stability and can therefore accommodate another electron and thus acquire a negative charge. The superfluidity of stability is not, however, great enough for them to accommodate two electrons so that we should not expect to find any atoms with a double negative charge.

In the experiments with positive rays the atom of neon which has eight electrons in the outer layer has never been observed with a negative charge, while negative charges are common on atoms of hydrogen, chlorine, carbon and oxygen. No atoms have been observed carrying two negative charges.

It is remarkable that though carbon and oxygen, the neighbours on either side of nitrogen, readily acquire negative charges, nitrogen itself is very rarely observed with a negative charge. It was thought for a long time that the nitrogen atom never carried a negative charge, recently, however, I have observed in more intense discharges a faint line on the positive ray photograph corresponding to the negatively charged nitrogen atom, it is, however, very feeble in comparison with the adjacent lines due to negatively charged carbon and oxygen, respectively. A calculation of the work required to remove the additional electron from a negatively charged nitrogen atom shows that it is very small in comparison with that required to remove the additional electrons from negatively charged atoms of carbon or oxygen, so that a negatively charged nitrogen atom would easily lose its charge and so be difficult to detect.

Again the only negatively electrified atoms we can observe by the positive ray method are those which have previously been positively charged, *i.e.*, those which at one time have lost an electron. . If such atoms, when they regain electrons, are in the condition we have ascribed to "active nitrogen" the electrons they regain will be far out from the centre of the atom and so will be very easily detached. Thus very few of these atoms could be expected to retain the electrons necessary to give them a negative charge.

There are some other interesting results which follow at once from the view we have taken of the constitution of the atom. The first we shall consider is the change in the chemical properties produced by electrifying the atom. Let us take the oxygen atom as an example, it has six electrons in the outer layer, and we may anticipate the results to be given in the next chapter by saying that its valency is determined by the number of electrons in this layer. When the oxygen atom is positively electrified it has lost one or more electrons. If it is electrified so that it carries one unit of positive charge, the unit of charge being that carried by an electron, it must have lost one electron, so that the atom will only have five electrons in the outer layer, the same number as there are in a neutral atom of nitrogen. Thus, if the valency depends on the number of electrons in the outer layer, the valency of oxygen carrying a unit charge of electricity ought to be the same as that of a neutral atom of nitrogen, *i.e.,* it ought to form the the compound OH_3, a compound having the molecular weight 19. This is confirmed by observation with the positive rays, when hydrogen and oxygen are present in the tube, a line corresponding to this molecular weight is frequently observed. Again, if the oxygen atom carries a double positive charge, and observations on the positive rays show that oxygen atoms with this charge are frequent when the electric discharge passes through gases, the atom must have lost two electrons and will be left with only four in the outer layer, the same number as in the outer layer of a neutral atom of carbon; hence the doubly charged oxygen atom ought to have the same valency as neutral carbon, and thus form the compound $(OH_4)++$. This compound would carry a double charge and the ratio of m/e would be 10. I have found[1] in the positive ray spectrum, lines having this value of e/m when both oxygen and hydrogen were in the discharge tube.

Again the atoms of the inert gases which have eight electrons in the outer layer, would, if they acquired one unit of positive charge, have lost an electron and would only contain seven electrons in the outer layer. This is the number in the outer layer of a neutral halogen atom. The positively electrified atoms of the inert gases could thus like the neutral atoms of the halogens combine with one atom of hydrogen and thus the compound NeH would be possible if it carried a unit charge of positive electricity.

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[1] *Proc. Roy. Soc.,* 101, p. 290.

The molecular weight of this would be 21 and a line corresponding to a carrier with this molecular weight has been observed by Aston. The neon atom can, as observations on the positive rays show, lose two electrons, in this state it could combine with two atoms of hydrogen, or one of oxygen, the first of these molecules would have the value $m/e = 11$, and the second $m/e = 18$; the first could not be distinguished from the isotope of neon atomic weight 22 with a double charge, and the line due to the second would be identical with that due to water, so that the positive rays could not afford convincing evidence of the existence of these compounds. If we turn to negatively electrified atoms, a negative electrified chlorine atom would have eight electrons in the outer layer, it would resemble the neutral atom of an inert gas and so would not be able to enter into chemical combination. It would seem as if it ought not to be very difficult to determine this point by direct experiment.

The negatively electrified chlorine atom has the same number of electrons as a neutral atom of argon, both having eight in the outer layer. It might therefore be expected to resemble argon not merely in its chemical properties, but also in the nature of its spectrum. The spectra would not be identical, for the positive charge binding the electrons together would be greater for argon than for chlorine. The similarity in the arrangement of the electrons might be expected to lead to similarities in the spectra of negatively electrified chlorine atoms and neutral argon atoms. Again, a positively electrified potassium atom has lost an electron and so would contain the same number of electrons as a negatively electrified chlorine atom or a neutral argon one. Thus we should expect the spectrum of positively electrified potassium atoms to show similarities both with that of negatively electrified chlorine atoms and with neutral argon atoms. Professor Zeeman and Mr. Dik[2] have compared the red spectrum of argon, which is the one due to the neutral atom, with the spectrum due to positively electrified potassium atoms and have found some exceedingly interesting points of resemblance. It is easier to observe the spectra due to positively electrified atoms than those due to negatively electrified ones, for in the latter case we should have to observe the spectrum they give out on receiving the negative charge, any attempt to stimulate them to luminescence afterwards would probably result in their destruction.

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[2] *Proc. Amsterdam Akademie*, 25, pt. 3 and 4.

Similarly positively electrified oxygen atoms might be expected to give spectra resembling those of neutral nitrogen atoms and positively electrified nitrogen atoms show similarities with neutral carbon atoms.

THE SIZE OF ATOMS.

By the radius of an atom we mean the distance of the electron in the outer layer from the centre of the atom. Let E be the central positive charge and

$$\frac{Ee}{r^2} - \frac{e^2C}{r^3} \tag{4}$$

the attraction between this charge and an electron at a distance r, e is the charge on the electron and $eC = cE$ where c is the quantity introduced in the expression for the same force (formula (1)), c is the distance at which the force between the positive charge and the electron changes from attraction to repulsion.

Then for the equilibrium of an electron on the outer layer we have

$$\frac{Ee}{r^2} - \frac{Ce^2}{r^3} = \frac{S_n}{4r^2}e^2 \tag{5}$$

where $S_n = \Sigma\frac{1}{\sin\theta}$, 2θ being the angle subtended at the centre of the atom by a pair of electrons and $\Sigma\frac{1}{\sin\theta}$ means that the sum of the values of $1/\sin\theta$ for each pair of electrons is to be taken. We get from this equation

$$r = \frac{C}{\frac{E}{e} - \frac{S_n}{4}} \tag{6}$$

The values of r for the lighter elements are given in the third column of Table IV. The fourth column is the value of r on the assumption that C is a linear function of the atomic weight, given by the equation $C = aN + b$, where N is the atomic weight and a and b constants.

Thus, taking the elements from lithium to neon, we see that the radius of the outer layer is greatest for the light elements and diminishes rapidly at first and then very slowly to the end of the period. When we pass from neon, the last element in this period, to sodium, the first in the next, there is a large increase in the radius. The sodium atom will have a larger radius than the lithium one, the ratio of the two will depend on the ratio of *a* to *b*, if *a* were zero the radii would be equal.

TABLE IV.

Element.	N	E/e	S_n	r	r
Hydrogen	1	1	0	C_H	$a + b$
Lithium	7	1	0	C_{Li}	$7a + b$
Beryllium.	9	2	1	$4C_{Be}/7$	$5.14a + .57b$
Boron	11	3	2.3	$4C_{Bo}/9.7$	$4.52a + .412b$
Carbon	12	4	3.66	$4C_C/12.3$	$3.88a + .322b$
Nitrogen	14	5	5.2	$4C_N/14.8$	$3.78a + .270b$
Oxygen	16	6	6.68	$4C_O/17.3$	$3.69a + .23b$
Fluorine	19	7	8.08	$4C_F/19.9$	$3.8a + .21b$
Neon	20	8	10.1	$4C_{Ne}/21.9$	$3.63a + .182b$
Sodium	23	1	0	C_{Na}	$23a + b$

The increase in the radius which occurs at sodium is followed by a continually diminishing radius until we reach argon; when we pass to potassium, the first element in the next period, there is again an increase. The radii of atoms in the same group like lithium, sodium, potassium, or fluorine, chlorine, bromine and iodine increase with the atomic weight of the element.

The relation between the radius of the atom and the atomic weight is such that the minima radii occur at the ends of the periods and not, as in Lothar Meyer's well-known graph, which has been reproduced in almost every text-book of chemistry, at the middle. Recent experiments have shown, however, that this graph does not accurately represent the relation. Gervaise le Bas,[3] says,

1. "There is a periodic relation between the atomic volume and the atomic weight of the elements."

2. There is a tendency for the atomic volume to diminish in each series as the atoms increase in weight, the smallest occurs in group 7.

3. There is a general increase in the atomic volumes of each group from series one onwards, that is in the direction of increasing atomic weight.

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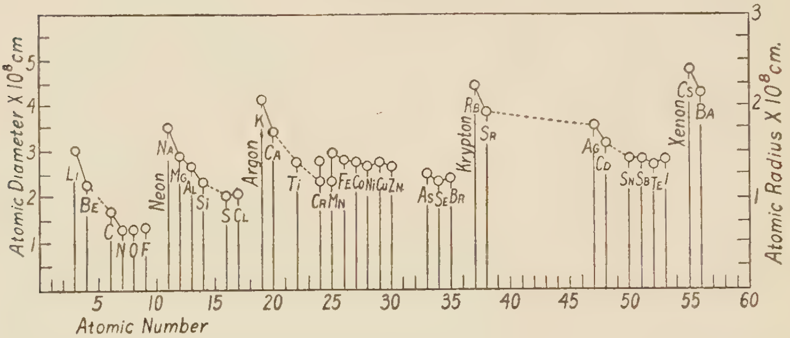
[3] "Molecular Volumes of Liquid Chemical Compounds," p. 237.

This is in entire agreement with the results we have just found. The same thing is beautifully shown by the experiments of W. L. Bragg[4] which give a curve (Fig. 1) for the atomic radii which in the period from lithium to neon agrees numerically very well with those deduced from the table (IV) given above, especially if b is small compared with a. The formula we have given would, unless a were very small compared with b, make the increase in atomic volume from lithium to sodium too great. According to Bragg the radius of the sodium atom is only about 1.2 times that of the lithium one. While if the formula could be stretched from one period to another the increase would be much greater unless a were very small compared with b. We shall see later on that the law of the inverse cube only holds within a limited range of r and that beyond a certain distance the force seems to vary as the simple law of the inverse square. An effect of this kind would prevent any large increase in the radius of the atom as we passed from one period to another, and we should expect to find, as is the case, that the agreement between theory and experiment is most marked for the lighter and smaller atom.

FIG. 1.



IONISING POTENTIAL.

Another quantity which has been the subject of a great many experiments is what is known as the ionising potential. This is the work required to detach an electron from the atom, expressed as the fall of the charge on an electron through this potential. We may remark that the work required to detach the electron must depend upon the way in which it is done, so that the ionising potential is not a perfectly definite quantity. Thus to take two extreme cases, we may suppose the electron removed so suddenly that the other electrons have no time to change their position before it is out of their range of action, or to take the other extreme we may remove it so slowly that the electrons are always in their position of equilibrium corresponding to the position of the electron which is being ejected. In the first case the work required to move the electron away from the central positive charge is $\frac{Ee}{r} - \frac{1}{2}\frac{Ce^2}{r^2}$, and the work done by the other electrons in ejecting it is $e^2/r_{12} + e^2/r_{13} + e^2/r_{14} \ldots$ where r_{12}, r_{13}, r_{14} are the distances of the ejected electron from the other electrons indicated by the suffixes 2, 3, 4. Now $r_{12} = 2r \sin\theta_{12}$ where $2\theta_{12}$ is the angle between the radii from the centre to the first and second electrons, and r is the distance of an electron from the centre, hence

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[4] *Phil. Mag.*, 40, p. 169, 1920.

$$\frac{e^2}{r_{12}} + \frac{e^2}{r_{13}} + \cdots = \frac{e^2}{2r}\left(\frac{1}{\sin\vartheta_{12}} + \frac{1}{\sin\vartheta_{13}} + \frac{1}{\sin\vartheta_{14}}\cdots\right)$$
$$= \frac{1}{2r} S_n \qquad (7)$$

The work required to remove the electron is thus

$$\frac{Ee}{r} - \frac{1}{2}\frac{Ce^2}{r^2} - \frac{e^2}{2r} S_n \qquad (8)$$

but from the equation of equilibrium

$$\frac{Ee}{r^2} - \frac{e^2C}{r^3} = \frac{e^2S_n}{4r^2}; \qquad (9)$$

hence if V is the ionising potential, Ve, since it is equal to the work required to remove the electron, is given by the equation

$$Ve = \frac{Ee}{2r} - \frac{3}{8}\frac{e^2S_n}{r}, \qquad (10)$$

if n is the number of electrons $E = ne$ and

$$V = \frac{e^2}{2r}\left(n - \frac{3}{4}S_n\right). \qquad (11)$$

Next take the case when the electron is removed so slowly that the system of electrons is always in equilibrium. The work required is the difference between the potential energy of the atom in its original state when it contains n electrons and in its final state when it contains $(n-1)$ electrons. The value of the former is

$$\frac{1}{2}\frac{ne^2}{r}\left(n-\frac{S_n}{4}\right) \tag{12}$$

that of the latter

$$\frac{1}{2}\frac{(n-1)e^2}{r_1}\left(n-\frac{S_{n-1}}{4}\right) \tag{13}$$

where r_1 is the radius of the atom when one electron has been removed.

For the equilibrium of the electrons in this state we have

$$\frac{Ee}{r_1^2}-\frac{e^2C}{r_1^3}=\frac{e^2S_{n-1}}{4r_1^2} \tag{14}$$

from the equilibrium of the atom in its original state we have

$$\frac{Ee}{r^2}-\frac{e^2C}{r^3}=\frac{e^2S_n}{4r^2} \tag{15}$$

hence

$$\frac{1}{r_1}=\frac{1}{r}\frac{\left(1-\frac{S_{n-1}}{4n}\right)}{1-\frac{S_n}{4n}} \tag{16}$$

and the difference between the potential energies is

$$\frac{1}{2}\frac{e^2}{r}\left\{n\left(n-\frac{S_n}{4}\right)-(n-1)\frac{\left(n-\frac{S_{n-1}}{4}\right)^2}{n-\frac{S_n}{4}}\right\} \tag{17}$$

$$=V_2\,e$$

if V_2 is the ionising potential for slow ionisation. In calculating these ionising potentials we have assumed that the law of force between the positive charge and the electron was expressed by $\frac{Ee}{r^2}-\frac{e^2C}{r^3}$ at all distances, there is evidence, however, that the repulsive term varying inversely as the cube of the distance has only a limited range of action and that beyond this range the force varies strictly as the inverse square of the distance. If we suppose that the range of the repulsive force is $\rho Ce/E$, then the work done in taking an electron from a distance r to an infinite distance will be

$$\int_r^\infty \frac{Ee}{r^2}\,dr - \int_r^{\rho Ce/E} \frac{e^2C}{r^3}\,dr$$
$$= \frac{Ee}{r} - \frac{1}{2}e^2\frac{C}{r^2} + \frac{1}{2}\frac{E^2}{\rho^2 C}$$

In calculating the ionising potential, we have neglected the last term and so have underestimated its value. Neglecting this correction, the ionising potentials for the elements whose outer layers contain 1, 2, 3, 4, 5, 6, 7, 8 electrons, respectively, are given in the following table. r_1 is the radius of the outer layer of the one electron atom, r_2 that of the two electron atom and so on. The third column gives the potential in volts when the values of r_1, r_2 . . ., given by W. L. Bragg (*loc. cit.*), are substituted in column 2.

TABLE V.

Number of Electrons in Outer Layer.	Ionising Potential for Quick Ionisation.		
1	$\frac{1}{2}\, e^2/r_1$	4.8	Lithium
2	$.625\, e^2/r_2$	8.1	Beryllium
3	$.633\, e^2/r_3$		
4	$.63\, e^2/r_4$	11.8	Carbon
5	$.54\, e^2/r_5$	12	Nitrogen
6	$.52\, e^2/r_6$	12	Oxygen
7	$.5\, e^2/r_7$	10.5	Fluorine
8			

These values apply to the ionisation of the atom and not of the molecule. In experiments on the ionising potential it is the value for the molecule and not for the atom which is in general determined.

SPECIFIC INDUCTIVE CAPACITY.

Further information about the atom is afforded by the study of the specific inductive capacity of the gas. We shall proceed to find the value of the specific inductive capacity of atoms containing different numbers of electrons.

The case of the one electron atom is exceptional because such an atom in its undisturbed state has a finite electrical moment, it will therefore tend to set in an electric field and this will give rise to a term in the specific inductive capacity independent of the displacement of the electrons inside the atom by the electric field; this term will vary rapidly with the temperature.[5] In addition to this effect due to the setting of the atoms there will be an effect due to the displacement of the electrons relative to the central core under the action of the electric field; this effect will be present in atoms containing more than one electron. The effect due to setting is absent when the normal atom has no finite electrical moment.

TWO ELECTRON ATOM.

If a is the distance of either of the electrons from the centre of the normal atom, X the external electric force, then if this force is in the direction of the line joining the electrons, the displacement δx of either of the electrons in the direction of the force is given by the equation

$$e\delta x = \frac{4}{5} a^3 X \tag{19}$$

This displacement of the electron relative to the positive charge endows the atom with an electric moment $2e\delta x$, and if N is the number of atoms per cubic centimetre, the electric moment per cubic centimetre is

$$N \frac{8}{5} a^3 X \tag{20}$$

hence if K_1 is the specific inductive capacity of these atoms

$$K_1 - 1 = 4\pi N \frac{8}{5} a^3 \tag{21}$$

If the electric force acts at right angles to the line joining the electrons, then

$$e\delta x = 4 a^3 X \tag{22}$$

and K_2, the specific inductive capacity for atoms orientated this way, is given by the equation

$$K_2 - 1 = 4\pi N \times 8a^3 \tag{23}$$

If the atoms in the gas are uniformly orientated, the specific inductive capacity K of the assemblage will be given by the equation

$$K = \frac{K_1 + 2K_2}{3}$$

or

$$K - 1 = 4\pi N a^3 \times \frac{8 \times 11}{15}. \tag{24}$$

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[5] *Phil. Mag.*, 27, p. 757.

The value of the specific inductive capacities for gases whose atoms contain from two to eight electrons is given in Table VI, which has been calculated by Miss Woodward.

It will be noticed that if K is the specific inductive capacity of a gas in the atomic condition, $K - 1$ is equal to ga^3, where a is the distance of the outer electrons from the centre of the atom, g is a quantity primarily depending on the number of electrons in the outer layer. For elements belonging to the same family the number of electrons in the outer layer and therefore g is constant, so that the ratio of specific inductive capacities of two members of one family should be the same as the ratio of the volumes of the atoms. Cuthbertson has pointed out that there are some remark-

TABLE VI.

Specific Inductive Capacity of Atoms with Two to Eight Electrons.

No. of Electrons	Arrangement.	K.	Mean value of K.
8	Cube	$1 + 4\pi r^3 N \cdot 4{\cdot}338$	$1 + 4\pi r^3 N \cdot 4{\cdot}338$
8	Twisted cube force perpendicular to sq. face	$1 + 4\pi r^3 N \cdot 4{\cdot}27$	
7	One layer, force perpendicular to plane of pentagon	$1 + 4\pi N a^3 \cdot 3{\cdot}605$	$1 + 4\pi a^3 N \cdot 4{\cdot}29$
7	One layer, force parallel to plane of pentagon	$1 + 4\pi N a^3 \cdot 4{\cdot}634$	
6	One layer	$1 + 4\pi N r^3 \cdot 4{\cdot}269$	$1 + 4\pi r^3 N \cdot 4{\cdot}269$
5	One layer, force perpendicular to plane of triangle	$1 + 4\pi a^3 N \cdot 4{\cdot}655$	$1 + 4\pi a^3 N \cdot 4{\cdot}236$
5	One layer, force parallel to plane of triangle	$1 + 4\pi a^3 N \cdot 4{\cdot}027$	
4	Tetr hedron	$1 + 4\pi N r^3 \cdot 3{\cdot}9$	$1 + 4\pi N r^3 \cdot 3{\cdot}9$
3	Triangle, force perpendicular to plane of triangle	$1 + 4\pi N r^3 \cdot 5{\cdot}203$	$1 + 4\pi N r^3 \cdot 4{\cdot}39$
3	Triangle, force parallel to plane of triangle	$1 + 4\pi N r^3 \cdot 3{\cdot}981$	
2	Force perpendicular to line of electrons	$1 + 4\pi N r^3 \cdot 8$	$1 + 4\pi N r^3 \cdot 5{\cdot}87$
2	Force parallel to line of electrons	$1 + 4\pi N r^3 \cdot 1{\cdot}6$	

ably simple relations between the refractivities and therefore between the values of $K - 1$, for consecutive elements in the same family. This is shown by Table VII given by Cuthbertson and Prideaux.[6]

Thus for these four families the ratio of the refractivity of an element in the first period to the corresponding element in the second and third periods is the same for all the elements. We have seen that for members of the same family the ratio of the values of $K - 1$ is equal to the ratio of the volumes of the elements. So from these experiments we arrive at the interesting deduction that, on passing from one period to the next, the volumes of all the atoms are increased in the same proportion.

TABLE VII

Element.	Refractivities.	Approximate Ratio.
Helium	72.0	½
Neon	137.4	1
Argon	568.	4
Krypton	850.	6
Xenon	1378.	10
Fluorine	195	1
Chlorine	768	4
Bromine	1125	6
Iodine	1920	8
Nitrogen	297	1
Phosphorus	1197	4
Oxygen	270	1
Sulphur	1101	4

Some confirmation of this is furnished by the determinations by W. L. Bragg[7] of the diameters of the atom of the various elements, these were made by measuring by the Röntgen-ray method the distance between the metal and the negative element in a series of salts. In these the atoms of the negative elements are probably negatively charged and are not in the state of neutral atoms. For the electronegative elements the diameters are as follows:

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[6] *Phil. Trans.*, A, 205, p. 319.

[7] *Phil. Mag.*, 40, p. 169.

Å is 10^{-8} cm.

F = 1.35 Å
Cl = 2.10 Å
Br = 2.38 Å
I = 2.8 Å

O = 1.30 Å
S = 2.05 Å
Se = 2.35 Å

C = 1.54 Å
Si = 2.35 Å

For the ratio of the diameters, we have

Cl/F = 1.55   Br/F = 1.76   I/F = 2.07
S/O = 1.57   Se/O = 1.8
Si/C = 1.53

For these elements, which are all electronegative ones, there seems thus some evidence from direct measurements that the ratio of the diameters of the atoms of corresponding elements in two periods is constant. It does not, however, apply to the electropositive elements like the alkali metals. Thus, for example,

Na/Li = 1.185   K/Li = 1.38   Rb/Li = 1.5
Mg/Be = 1.24   Ca/Be = 1.5   Sr/Be = 1.7   Ba/Be = 1.8

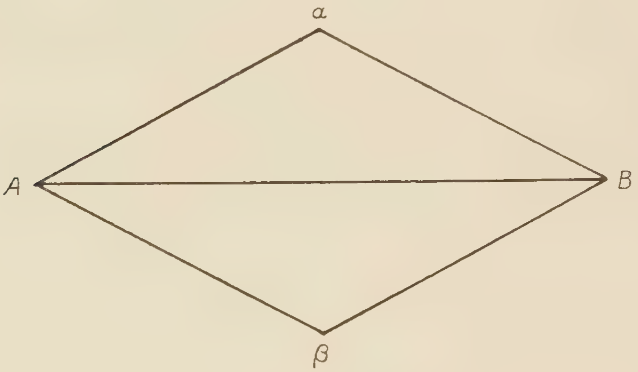
Thus the increase in the size of the atoms of corresponding metals in different periods is not nearly so large as in that of the atoms of corresponding electronegative elements.

CHAPTER II.

THE COMBINATION OF ATOMS TO FORM MOLECULES.

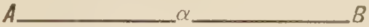
We shall begin by considering molecules in the gaseous state, where each molecule is separated so far from its neighbours that it may be regarded as an individual and not as merely forming a brick in a much larger structure. Indeed, the term molecule when applied to the solid state is quite ambiguous without further definition; for example, from many points of view we can consider quite legitimately the whole of a large crystal as forming a single molecule. It is natural to expect that when the atoms are crowded together as in a solid, where each atom may come under the influence of a large number of neighbours, the arrangement of the electrons relatively to the atom may differ substantially from that in a gaseous molecule.

Fig. 2.



Let us begin with the simplest case, that of the union of two similar atoms each containing one electron. We see that if the atoms and electrons are arranged as in Fig. 2, where *A* and *B* are the atoms and α and β the electrons, the mutual repulsion of the electrons may be balanced by the attraction of the positive charges on the electrons; and the mutual repulsions of the similarly electrified atoms by the attractions of the electrons. Thus we may regard the electrons in the atom as acting like hooks by which one atom gets coupled up with another. As the atoms are held together by the attraction of the pair of electrons α, β, the presence of two electrons between the atoms may be taken as the physical interpretation of what is called a bond by chemists. In this example and in general, two electrons go to each bond. There are, however, cases such as that of a positively electrified molecule of hydrogen (so frequently detected in positive-ray photographs) where a single electron is able to bind two atoms together. The arrangement being that represented in Fig. 3.

FIG. 3.



The dimensions and shape of the parallelogram represented in Fig. 2 will depend on the law of force between two positive charges at atomic distances as well as upon that between a positive charge and an electron. If $e^2\varphi\left(\frac{c}{r}\right)$ is the attraction between a positive charge e and an electron with equal charge separated by a distance r and $e^2\psi\left(\frac{c^1}{r}\right)$ the repulsion between two positive charges at a distance r, then if $A\alpha = r$ and $< A\alpha\beta = \vartheta$, we have for equilibrium

$$2e^2\varphi\left(\frac{c}{r}\right)\mathrm{ccs}\,\vartheta = \frac{e^2}{4r^2\cos^2\vartheta} \qquad (25)$$
$$2e^2\varphi\left(\frac{c}{r}\right)\sin\vartheta = e^2\psi\left(\frac{c^1}{2r\sin\vartheta}\right)$$

Though the distance of an electron from its atom will obviously be not quite the same in the molecule as in the atom, we should expect that the differences would not be very large. For if they were, work would have to be done at some stage in the act of combination comparable with that required to ionise an atom, as this work is much greater than the equivalent of the heat developed by the union of the atoms to form a molecule we could not expect atoms under these conditions to combine to form molecules except in the presence of a very efficient catalyst.

Let us now pass to the case where each of the atoms contains two electrons. If only one pair of electrons is used up in uniting the atoms, the arrangement would be that represented in Fig. 4, where the Greek letters represent the electron. In the language of chemists this would be expressed by saying that the atoms were united by a single bond and the molecule would be expressed by the formula $-A-B-$. The electrons α' and β' would enable this molecule to link up with other molecules so that it would not be saturated. If, however, all four electrons are used in coupling up the atom, they will be at the corners of a square in a plane bisecting *AB* at right angles.

The system of four electrons instead of two between the positively electrified atoms may be regarded as the physical equivalent of what the chemists call a double bond. Inasmuch as the equilibrium of four electrons in one plane, when their displacements are not confined to that plane, requires very strong restoring forces to make it stable, we should not expect the double bond to be permanent when the positive charges which exert the restoring force are as small as in this case, where their sum is only equal to the sum of the charges on the four electrons.

FIG. 4.

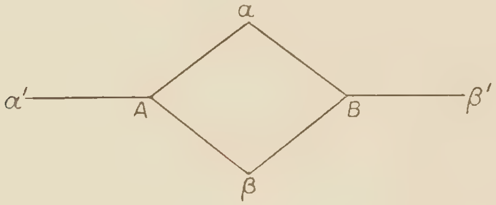
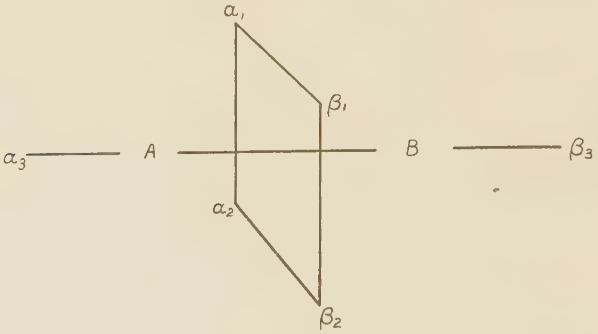


FIG. 5.



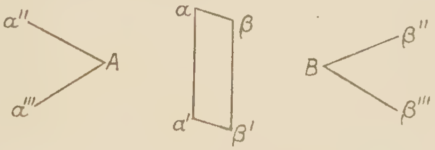
For the union of two tri-electron atoms, if all the electrons were used to couple up the atoms, there would be a hexagonal ring of electrons in a plane bisecting *AB* at right angles, as this ring requires a greater positive charge than that of three units on each side to keep it in stable equilibrium it would be unstable. The most probable arrangement of the electrons is the octahedral one shown in Fig. 5 with four electrons between the atoms and two on the line *AB*; this would be represented symbolically by the formula $-A=B-$. The end electrons would enable it to bind other atoms so that the molecule would not be saturated.

FOUR-ELECTRON ATOMS.

These may form a molecule in which the electrons are as represented in Fig. 6, four electrons are between *AB* and the other four form two pairs beyond the extremities of the line *AB*.

A peculiarity of the arrangement in Fig. 6 is that the molecule has four free electrons the same as the original atom, thus other atoms can be coupled up with the molecule, and we might have a chain of atoms, each atom being at the centre of a parallelipiped of eight electrons. We can show that a long chain of such atoms would be unstable, but it is evident that the four-electron atom is one peculiarly suited for forming complexes containing several atoms. The carbon atom has four electrons in its outer layer and thus carbon atoms would have a great tendency to unite with each other. It is this tendency that is responsible for the science of Organic Chemistry. I may point out in passing that we can obtain from the study of positive rays direct evidence of the coalescence of carbon atoms. For on a positive-ray photograph of benzene I found lines corresponding to C_1, C_2, C_3, C_4, C_5, where C_1 represents a carbon atom; C_2, a carbon molecule; C_3, a carbon triplet, and so on.

FIG. 6.

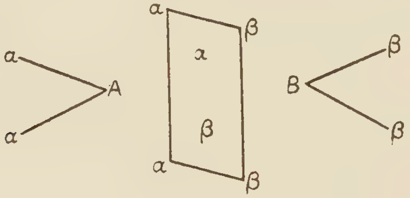


The form we have suggested for the electrons in the molecule of atoms of this type is represented symbolically by the formula $=A=B=$. When we come to the case of five-electron atoms we have to introduce new considerations. We have seen that eight is the maximum number of electrons which can be in stable equilibrium in a single layer under the action of positive charges whose aggregate cannot exceed the total charges carried by the electrons. With a five-electron atom we have ten electrons in the molecule, while the aggregate positive charge, in the molecule, is also ten, which is not sufficient to keep the ten electrons in stable equilibrium if spread over a single layer. A simple way of arranging the electrons is shown in Fig. 7. Midway between the positive charges are six electrons which keep the atoms together, four of them at the corners of a square forming the normal double bond, while two others are inside the square.

The remaining four electrons are arranged in pairs beyond the atoms *A, B,* respectively. Thus we have eight electrons surrounding two atoms and two electrons. The arrangement is somewhat like that suggested for the carbon molecule with the addition of two electrons near the centre of the molecule.

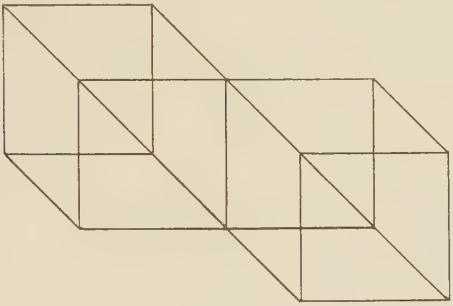
When each of the atoms contains six electrons the arrangement is as follows: There are four electrons forming the normal double bond between the atoms, and two other sets of four, one set beyond *A,* the other beyond *B.* Thus each of the two atoms may be regarded as being inside an octet of electrons, the two octets having four electrons in common. When each of the atoms contains seven electrons, we have fourteen electrons at our disposal. These may be arranged so that two of them form a single bond between the atoms while the remainder complete two octets with two electrons common to both, as is represented in Fig. 8. This, though a very symmetrical arrangement, is not the only conceivable one. For when the positive charges are large, as they are in this case, they might hold four or even more electrons in stable equilibrium, even though the electrons were very close together. Thus suppose there were a double instead of a single bond between the atoms, this would account for four electrons, leaving ten to be distributed outside. If these were distributed symmetrically, there would be five around each atom, so that each atom would be the centre of a layer containing nine electrons, four coming from the double bond and five from those

FIG. 7.



left over after the double bond has been provided for. Now nine electrons could not be in equilibrium if equally distributed under a central charge of seven, but if four of them are held close together in stable equilibrium under two positive charges, it is possible that there may be room for the other five to be so far apart that they can be kept in stable equilibrium by a positive charge of seven units.

FIG. 8.



It will be noticed that the molecules formed by the union of two atoms, each of which contains less than five electrons, have free electrons which are available for linking up with other molecules. The one-electron atoms could form chains as in Fig. 9. Thus the process of aggregation is not exhausted by the formation of the molecule; these molecules will form further aggregations and thus tend to get into the solid or liquid state. On the other hand, the molecules formed by atoms with five or more electrons form saturated systems and will not tend to aggregate further. This agrees with the properties of the elements; for Li, Be, Bo, and C, whose atoms contain less than five electrons, are solids, while N, O, F and Ne, whose atoms contain five or more electrons, are gases.

FIG. 9.

A——α——B——β——C——γ

From the consideration of the arrangements of the electrons in the different molecules, we see that for atoms containing four and five electrons we can regard the electrons in the molecule as distributed over a single layer not very far from spherical, when, however, we reach the six-electron atom the electrons in the molecule form two cells, and a surface which would contain them all would have to be very elongated. We get some confirmation of this result from the study of the scattering of polarised light by gases. The theory of such scattering shows that the light scattered by a single electron in a direction at right angles to the incident beam is completely polarised and can be extinguished by a Nicol prism. The same thing is true when the light is scattered by a perfectly symmetrical body such as a sphere. If the scattering body is not perfectly symmetrical, if, for example, it is elliptical instead of spherical, the scattered light is never completely polarised and therefore cannot be entirely quenched by a Nicol. The ratio of the minimum to the maximum intensity of the light seen through a Nicol would be zero for a spherical body, but would be finite for an ellipsoid and would increase with the ellipticity. The value of this ratio may be taken as an indication of the deviation of the scattering body from sphericity. The scattering of light by molecules is due to the electrons in the molecules; we should expect that an arrangement of electrons in one shell would approach more closely to the spherical arrangement than an arrangement in two cells, and that two cells would approximate to the spherical more closely than three. Thus the ratio of the minimum to the maximum intensity of the scattered light should increase with the number of cells. Lord Rayleigh[8] has determined the value of this ratio for several gases with the results given in the following table:

Gas.	Ratio Expressed as a Percentage.
Argon	.46
Hydrogen	3.83
Nitrogen	4.06
Oxygen	9.4
Carbon Dioxide	11.7
Nitrous Oxide	15.4

We see how small this ratio is for the symmetrical distribution of electrons round the argon atom. A striking feature of the table is the great jump between nitrogen and oxygen. We have seen that the passage from nitrogen to oxygen corresponds to the transition from an arrangement of the electrons in one cell to one in two cells, and thus involves a great loss in symmetry. The electrons in carbon dioxide and nitrous oxide require three cells for their arrangement and thus are less symmetrical than those in the oxygen molecule.

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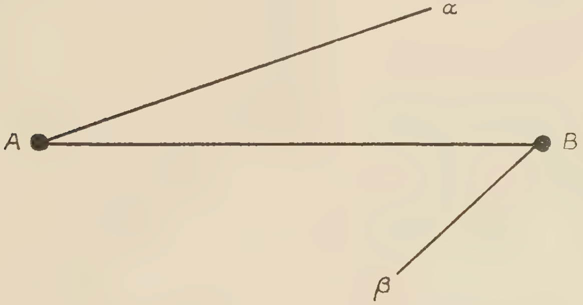
[8] *Proc. Roy. Soc.*, **98**, p. 57.

COMBINATION OF DIFFERENT ELEMENTS, CHEMICAL COMPOUNDS.

We may apply considerations similar to those we used to explain the formation of molecules of an element by the union of two similar atoms to the union of two different atoms to form the molecule of a compound.

Let us consider, for example, the union of a seven-electron atom with a one-electron atom. Suppose that *A* is the centre of the first atom, *B* that of the second.

FIG. 10.



Let α be an electron in the first atom, β one on the second. Then if *B* and β place themselves somewhat as in the figure, the attractions the two electrons exert on *A, B* may keep these together in spite of their mutual repulsions, while the electrons are kept in equilibrium by the attraction upon them of the atoms *A* and *B*. The addition of β to the seven electrons already round *A* will raise the number in the outer layer of *A* to eight. Now suppose we attempt to attach another atom *B'* to *A*, this would introduce another electron into the outer layer round *A*, raising the number in this layer to nine. We have seen, however, that nine electrons in one layer cannot be kept in stable equilibrium by a positive charge of nine units; in this case nine units are all we have at our disposal and two of these are outside the layer. The outside ones will make the arrangement of electrons more stable than it would be in their absence. They will not, however, increase the stability more than they would if they were inside, and even in that case they could not make the arrangement stable. Thus *A* cannot hold a second atom of the type B, so that the compound AB_2 is impossible and that represented by AB is saturated. Thus, if B with its one electron is taken as the type of a monovalent atom, like hydrogen, A with its seven electrons would also be monovalent, and would in this respect act like fluorine. The electrons in the molecule HF would form a layer round the centre of the fluorine atom with the positive part of the hydrogen atom outside. Let us now suppose that A is a six instead of a seven-electron atom and let an atom of B get attached to it in the way we have supposed. This will raise the number of electrons in the layer round A to seven, so another atom can be attached before the number of electrons in the outer layer is raised to eight and the limit of stability reached. Thus A could form the unsaturated compound AB and the saturated one, AB_2, but A could not combine with more than two atoms of B. Thus A with its six electrons would behave like the atom of a divalent element, say oxygen.

In a similar way we see that if A contained five electrons it would form the unsaturated compounds AB and AB_2 and the saturated one AB_3. Thus A would behave like a trivalent element, nitrogen.

In this way we see that when A acts as the centre round which the layer of electrons is arranged, it behaves like an element whose valency is equal to (8 − number of electrons in the outer layer of the atom A).

There is, however, another way in which the atoms might combine, in this A, instead of receiving electrons from other atoms, might give up electrons to help to form a layer round another atom. Take, for example, a two-electron atom B, by using one of its electrons it can attach itself to a seven-electron atom and still have one electron free. It can use this free electron to bind itself to another seven-electron atom and thus form the compound BF_2, where F represents an atom of such an element as fluorine. Thus in this type of compound the atom with its two electrons would behave like a divalent element. A three-electron atom would be able to bind three atoms of fluorine and so on. In this type of compound the atom under consideration is acting, so to speak, as a giver and not as a receiver of electrons. The valency of the atom when acting in this way is equal to the number of its electrons. The electron theory thus, as I pointed out long ago,[9] leads in a very natural manner to an explanation of valency and it suggests conclusions very similar to those advanced by Abegg and Bödlander,[10] who ascribed to each element two valencies according as it was combined with a more electronegative or more electropositive element, the sum of the two valencies always being eight. We have in some of the elements notable instances of two valencies; take nitrogen as an example, whose atoms contain five electrons in the outer layer. If this combines with hydrogen, three atoms of hydrogen will saturate it, as they will bring the number of electrons in the layer round the nitrogen up to eight, the limiting number, thus in the compound NH_3, the nitrogen behaves as a trivalent element. But suppose that instead of combining with a hydrogen atom it combines with a chlorine one, which we assume to have seven electrons in the outer layer. One of the electrons from the nitrogen atom might join the layer round the chlorine one, bringing the number of electrons in the latter up to eight, and leaving four in the nitrogen atom. These four electrons can link up with four hydrogen atoms which will bring the number of electrons in the layer round the nitrogen atom up to eight, the limiting number. We thus get the compound NH_4Cl. The arrangement of the electrons being as represented in Fig. 11. As the chlorine nucleus has a positive charge of seven and is surrounded by a layer containing eight electrons, the atom Cl in this compound has a unit negative charge. Since there is a positive charge of five on the nitrogen nucleus and one of four on the four hydrogen atoms, there are nine positive charges on the system NH_4, which contains eight electrons; there is thus a balance of one positive charge on the system repre-

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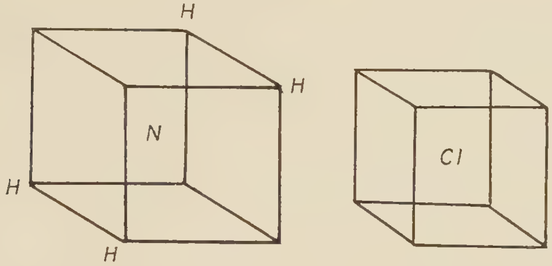
[9] *Phil. Mag.*, [6] 27, p. 757 (1914).

Fig. 11.



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[10] *Zeit. Anorg. Chem.*, 20, p. 453 (1899); 30, p. 330 (1904).

sented by NH_4, so that NH_4Cl would, when electrolysed, give NH_4 and Cl as ions.

Again each of the five electrons of the nitrogen atom might go off to complete the tale of eight electrons round each of five chlorine atoms forming the compound NCl_5; though this substance does not seem to have been prepared, the corresponding compound PCl_5 is well known. The oxygen atom containing six electrons might attach itself to six atoms of chlorine and so be apparently hexavalent, as sulphur is in the remarkable compound SF_6, discovered by Moissan.

Carbon having four electrons in the outer layer has the same valency $4 = 8 - 4$, whether it is acting in either of the above-mentioned ways, hence the compounds CH_4, CCl_4. The kind of union between atoms which we have been considering requires two electrons to effect the bond, hence since we cannot have more than eight electrons round a central atom, four is the maximum number of atoms which can be bound by a single atom. There are in fact very few exceptions to this rule, the most conspicuous are the chlorides of some of the elements which have very variable valencies, such as $UrCl_5$ WCl_5, $MoCl_5$, which will be considered later.

Thus the considerations we have been discussing give a physical basis for the theory of valency in the extended form given by Abegg. The electron theory, however, is much more general than the laws of valency and points to the existence of compounds which are not in accordance with these laws. The electron theory states that any distribution of atoms and electrons in stable equilibrium is a possible compound and will be saturated provided that each electronegative atom is surrounded by a layer containing eight electrons.

Let us consider, as an example, carbon monoxide, CO; this, according to valency laws, is an unsaturated compound, the gas is, however, remarkably inert and only liquefied with great difficulty, so that its physical properties give no support to the view that it is a highly unsaturated gas. In CO there are ten electrons to be arranged the same as in N_2, and we may therefore expect that a similar arrangement to that represented in Fig. 7 would furnish a stable and permanent molecule. As the positive charge on the carbon is not the same as that on the oxygen, the cell will not be so symmetrical as that of the nitrogen molecule. It is interesting to note that, as Langmuir has pointed out, some of the physical properties of CO are very similar to those of N_2. If this is the constitution of the molecule of CO, it explains why we do not get CH_2 as a saturated substance, as the ordinary valency theory would lead us to expect. There are only six available electrons in CH_2 and these are insufficient to produce a completely saturated layer. It is important to point out that we distinguish between the molecule of carbon monoxide and that of the carbonyl radicle CO. In the latter we suppose that two out of the four electrons of the carbon atom have gone to unite it with the oxygen and to make up the eight electrons required to form the layer round the oxygen atom, while the other two are free to join up with other electrons. Thus while the molecule of CO is represented by Fig. 7, that of the carbonyl radicle is represented by Fig. 12.

FIG. 12.

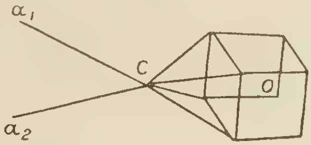
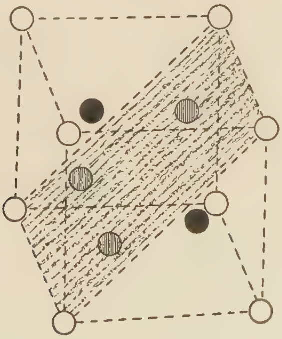


FIG. 13.



Another molecule which may have a somewhat similar constitution to that of CO is NO, Fig. 13. The molecule contains eleven electrons, if we take eight of these to form the outer layer we are left with three, these by taking up positions between the atoms of nitrogen and oxygen inside the outer layer may help to keep these atoms together. The molecule of nitrogen monoxide is not the only form in which the combination NO occurs; it can also exist as the radicle NO, and just as we suppose the carbonyl radicle to have a different configuration from that of the molecule CO, so we suppose that the radicle NO has a configuration in which eight electrons form a cell round the oxygen, the nitrogen atom is surrounded by a layer of seven electrons made up of the three electrons left over after two have been supplied to the oxygen octet; the other four form part of the layer round the oxygen atom. The layer round the nitrogen requires another electron to saturate it and will thus act like a univalent atom. The three electrons left over from the five nitrogen electrons after two have been used to saturate the cell round the oxygen atom might be used to bind three hydrogen ions and thus it is possible that under certain circumstances this radicle might be trivalent.

Nitrogen monoxide is an example of the rare type of molecule where the number of electrons in the molecule is odd. Other examples of this type are NO_2 and ClO_2. If we suppose that for stable substances an octet of electrons is formed round each of the heavier atoms in the molecule, then if the number of electrons is odd, some of these octets must have an odd number of electrons, either one or three, in common. If we suppose the octets are cubes, they could not have three electrons in common, though they could have one, the two cubes having a corner in common. If, however, the electrons are arranged in twisted cubes instead of the ordinary cubes, two octets might have 1, 2, 3 or 4 electrons in common, since twisted cubes have triangular as well as square faces and thus we might have molecules containing an odd number of electrons with a less exiguous connection between the atoms than that furnished by a single corner common to two octets. The three-electron contact would account for the existence of a saturated compound with the formula ClO_2. We have here nineteen electrons and these might be accommodated in three octets if there was one double contact and one triple one.

Another problem in which the triple contact might come in, is the well-worn one of the benzene ring. In benzene C_6H_6 we have thirty electrons which have to be arranged in octets round six carbon atoms. The simplest and most symmetrical way of doing this is to have the six cells in contact round a ring with a threefold contact between each two. As two opposite triangular faces of the twisted cube are inclined to each other, this could be done without introducing much strain into the system. Models have been made by two of my students on this principle of a benzene ring and also of a naphthalene one. With this arrangement we have complete symmetry, and it is analogous to the Armstrong and Bayer or central theory of the benzene ring. The configuration corresponding to Kekules' conception of the constitution of the benzene ring would consist of three sets of pairs of cells, the cells in one pair having four-fold contact with each other, but only double contact with a cell in a neighbouring pair.

The three-contact view leads to results with regard to the constitution of addition compounds of benzene and the halogens which are in harmony with experience.

The process which we have just been describing by which two atoms *A*, *B* are united into a molecule *AB*, of a compound may be regarded as consisting in one or more of the electrons in the outer layer of *A* becoming a member of the outer layer of *B*. This is equivalent to one of the electrons in the outer layer of *B* becoming a member of the outer layer of *A*. Thus each atom lends electrons to the other to enable it to fill up its outer layer; the atoms share their electrons for this purpose and the electrons which they have in common tend to hold the two atoms together. I think it is desirable to emphasize this aspect of the question, to regard the union of the two electrons as a sharing of their electrons rather than as the robbery by one atom of the electron belonging to another. I doubt if there is any very large change produced in gaseous compounds by chemical combination in the distance of an electron from the centre of the atom to which it originally belonged. I do not mean that the distance remains unaltered, but only that there is no such change in distance as would warrant our saying that the electron was bound to *B* before combination and was free afterwards. To tear electrons from an atom requires a much larger amount of work than to separate a molecule into uncharged atoms, and though there may be a redistribution of the electric charges on the molecule, there is nothing which can fairly be described as ionisation. Thus to take a specific example we regard the constitution of a molecule of HF as consisting of a unit positive charge H outside an outer layer of eight electrons surrounding the fluorine atom with its positive charge of seven units, and though we may legitimately describe the molecule as consisting of a positively charged hydrogen atom and a negatively charged fluorine one, it does not follow, if the molecule were dissociated by a rise in temperature, that the product of dissociation would be a positively charged hydrogen atom and a negatively charged fluorine one. It would take much less energy to detach the positive hydrogen atom plus an electron than the positively charged hydrogen atom alone, so that the probable result of the dissociation would be a neutral hydrogen atom and a neutral fluorine one. This would not necessarily be the case if the dissociation were effected by a high-speed positive ray with an energy corresponding to many thousand volts, for then the hydrogen atom could receive energy far more than sufficient to detach it from the negative electron. The result to which we have been led that dissociation would yield neutral atoms is in accordance with experience, for we do not find that chemical changes in gases produced by a rise in temperature are accompanied by a rise in electrical conductivity unless the gases are in contact with hot metals, and in this case the increase in conductivity may be explained by thermionic effects. The absence of electrical conductivity in several cases of chemical action at moderate temperatures was investigated by Bloch,[11] who showed that the dissociation of arseniuretted hydrogen which takes place at low temperatures is not accompanied by any increase in the electrical conductivity. He also showed that many chemical actions which go on at low temperatures such as the oxidation of nitric oxide, the action of chlorine on arsenic, the oxidation of ether vapours, have little or no effect on the conductivity.

POLAR MOLECULES.

Though in the gaseous molecule we have not ionisation in the sense that the atoms of the molecules are free to move in opposite directions under the action of an external electric force, yet the disposition of the electric charges may be such that the molecules would tend to set in a definite direction under the action of such an electric force. The centre of the positive charges does not always coincide with that of the negative ones, so the molecule may have a definite electric moment. It is only in some type of molecules that this electric moment has a finite value. Thus in the symmetrical molecule formed by the union of two atoms of the same kind the centres of the positive and negative electric charges coincide and the molecule has no electrical moment.

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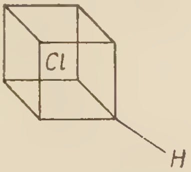
[11] *Ann. de Chimie et de Physique,* **22**, pp. 370, 441; **23**, p. 28.

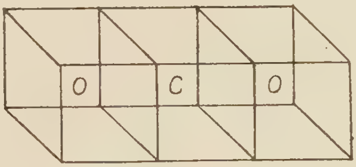
FIG. 14.



Whereas in a molecule like HCl, where the positive charge is outside the octet as in Fig. 14, the molecule has evidently a finite electric moment.

In other compounds such as CO_2, of which the arrangement is that in Fig. 15, there is complete symmetry. Thus, as I pointed out some years ago,[12] molecules may be divided into two types:

FIG. 15.



(*a*) Polar, those having a finite electric moment; (*b*) Non-polar, those for which the electrical moment vanishes.

These two types will have very different properties. If the molecule has a finite electrical moment, it will give rise to an electric field whose intensity will vary inversely as the cube of the distance, while if the electric moment vanishes the force due to the molecule will vary inversely as some higher power of the distance and will thus die away much more rapidly than the forces due to a polar molecule; the latter will have a more extensive stray field and will attract and be attracted by a much larger number of other molecules.

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[12] *Phil. Mag.*, 27, p. 757 (1914).

PHYSICAL TEST FOR POLAR MOLECULES.

We shall first describe a test based on physical principles by which we can separate the polar from the non-polar molecule and then see whether the molecules so separated show marked difference in their chemical properties.

The physical method for determining whether the molecule has a finite moment or not is the determination of the specific inductive capacity of the substances formed by the molecules, and if possible when the substance is in the gaseous state. The molecule with a finite moment will tend to set in a definite direction under the electric field, and this setting will contribute to the specific inductive capacity of the gas, hence such molecules will tend to give an abnormally high value to the specific inductive capacity. Again, since this setting of the molecule involves the rotation of the molecule as a whole, these will move so sluggishly that they will not be affected by vibrations as rapid as those of light waves in the visible spectrum.

Hence these molecules will not affect the refractive index in the visible spectrum while they will affect the specific inductive capacity. We should expect, therefore, that the substances formed by such molecules would depart widely from Maxwell's law that the square of the refractive index is equal to the specific inductive capacity. Again, since the setting of the molecules under the electric field will be hampered by the collisions with other molecules and as these collisions are more numerous and vigorous at high temperatures than at low, the specific inductive capacities of these substances will be affected by temperature and will diminish as the temperature increases. Bädeker[13] has determined the specific inductive capacities of many gases at varying temperatures, and it appears from his results that some of these gases, such, for example, as H_2O, NH_3, HCl, CH_3OH, exhibit all these characteristics, they have specific inductive capacities which are much greater than the square of the refractive index and which diminish as the temperature increases.

Taking this as the criterion, we can find whether the molecules have or have not finite electrical moments and in the following tables, derived from measurements made by Bädeker and other observers, of the specific inductive capacity of gases, various compounds are placed in one or other of two classes.

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[13] *Zeit. fur Physik Chem.*, 36, p. 305.

I.

Compounds which have a finite electrical moment.

H_2O
NH_3
SO_2
HCl
CH_3OH
C_2H_5OH
CH_3Cl
$CHCl_3$ (slight)

II.

Compounds which have not a finite electrical moment.

H_2
O_2
N_2
He
Cl_2
CO
CO_2
CS_2
CCl_4
C_6H_6
CH_4
N_2O

This list shows that the physical test we have applied separates the substances into two types which have great differences in their chemical properties. In the first type we have substances like water and alcohol which are good ionisers of salts or acids dissolved in them.

The substances in the first table are also those which, like water, ammonia, and alcohol, are conspicuous in forming complex compounds with other salts, such as the hydrates, alcoholates, ammoniates. Another property which differentiates the substances in Table I from those in Table II is that of giving electrification by bubbling. When air or other gases bubble through some liquids, *e.g.*, water, alcohol, acetone, the gas when it emerges is found to be ionised, *i.e.*, mixed with positive and negative ions. Little, if any, electrification is found when a gas bubbles through a liquid like paraffin oil or benzene. This is shown very clearly by the experiments of Bloch.[14] Liquids of the first type show electrification by bubbling, those of the second do not.

Molecules which contain the hydroxyl radicle OH, such as H_2O, CH_3OH, C_2H_5OH, are usually polar; other organic radicles, such as COOH, CO, CN, NO_2, also make the molecules of which they form a part polar. As the attraction of polar molecules extends over a much wider field than that of non-polar ones, we can understand why, though the hydrogen in saturated non-polar molecules such as CH_4, C_2H_6 is not oxydised by weak solutions of sulphuric acid or bichromate of potash, the hydrogen in polar molecules such as CH_3OH, CH_2O (formaldehyde), CHOOH, is oxydised under the same conditions.

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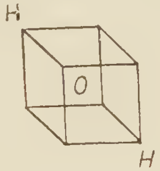
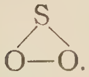
[14] *Ann. de Chimie et de Physique*, **23**, p. 28 (1911).

The fact that the polar molecule must be unsymmetrical gives us some information about the configuration of the electrons. One of the most interesting cases is that of water, which is conspicuous above all molecules for the possession of an electrical moment. Our first impression is that the structure of the water molecule should be that represented by Fig. 16, where the two hydrogen atoms are symmetrically placed with respect to the centre of the oxygen atom and the electrons are symmetrically distributed round the line joining the hydrogen atoms. This, however, cannot be right, for it would correspond to a molecule having no electrical moment. If the octet of electrons round the oxygen atom were situated at the corners of a cube, then there could be no question that a symmetrical arrangement of the hydrogen atoms with these atoms, respectively, attached to two electrons at the opposite ends of a diameter would be the position of equilibrium and this would correspond to a system having no electrical moment. If, however, the electrons were arranged at the corners of a twisted cube, no two electrons would be at opposite extremities of a diameter. Thus, if the positive atoms were attached to two electrons the system would be unsymmetrical and would have an electrical moment. Thus the electrical and chemical properties support the view that the electrons in the octet are at the corners of a twisted cube. The symmetrical position for the hydrogen atoms would, with the twisted cube, be when the positive hydrogen atoms are on the axis through the centre at right angles to the square faces. On this axis the positive atoms cannot be at a distance from the nearest electron less than half the diagonal of a square face. This distance is greater than would be necessary if the hydrogen atoms were placed close to the corners of the

FIG. 16.



octet. This increase of distance would correspond to an increase of potential energy which might make the arrangement unstable. It would appear from these considerations that there may be more than one form of water. Thus the two hydrogens might be joined (*a*) to two electrons on the same square face or (*b*) one of the hydrogens might be joined to an electron on one square face and the other hydrogen to an electron on the other. Similar considerations would apply to the hydroxides of the alkali metals, but we should hardly expect the want of symmetry in these to be as pronounced as in hydrogen for the reason that the radius of say an atom of sodium is greater than that of one of hydrogen, so that these atoms might be able to get into the symmetrical positions without their distance from the nearest electron being increased much beyond that between the atom and electron in the uncombined atom. The effect of increased size may be illustrated by comparing water with methyl ether, which may be regarded as water in which the hydrogen atoms are replaced by the larger CH_3 group. The specific inductive capacity of methyl ether and its dissociating power are very much smaller than those of water.

As another instance of the aid which considerations like these may give in determining the structure of the molecule, we may take the case of SO_2. The determination of its specific inductive capacity shows that it has a finite electrical moment. It is therefore more likely to be represented by one of the unsymmetrical formulas $S=O-O$, $O=S-O$, than by the more symmetrical one .

A molecule of a gas with a large electrostatic moment may itself promote combination between two gases, neither of which has molecules with a finite moment. Let us consider the effect of a molecule of this kind on the molecules of a gas near it. The intense electric field around this molecule will drag towards it the molecules around it; it will act as a nucleus round which the molecules of the other gas will condense. The nucleus will thus bring these molecules nearer together than they otherwise would be, and, if like chlorine and hydrogen, they can combine the presence of the nucleus, will assist combination. It seems possible that part of the action of water vapour in chemical combination may arise in this way, the interacting molecules crowding together so as to get into the strongest part of the electric field round the water molecules and thus getting into positions which are favourable for chemical combination.

In some cases the product of the chemical action will be active molecules with large moment. This will happen in the case of hydrogen and oxygen, or with hydrogen and chlorine, since the molecules of water and hydrochloric acid have a finite electrostatic moment. Here chemical combination promoted by the water vapour produces a fresh supply of active molecules and thus of nuclei which promote the combination. There will evidently be a tendency for mixtures of this type to become explosive. It is the intense electric field round a molecule with a finite electrostatic moment which causes the other molecules to condense round it. If, instead of a molecule with its electrostatic doublet, we had a charged ion, we should have a still more intense electric field and therefore might expect to get still greater condensation and more intense chemical action. The study of the conduction of electricity through gases gives us evidence of the existence of this condensation, as the ions in gases behave more like clusters than single molecules or atoms. It may be asked why is it that while molecules possessing finite electric moments are able to promote so markedly chemical action, yet the speed of these actions is not noticeably greater in ionised than in non-ionised gases, though in the former the ions must produce intense electrical fields? The answer to the question is, that in any ordinary type of ionisation the number of charged ions is very small indeed compared with the number of molecules of a foreign constituent of the gas, even when the constituent is present as the merest traces. Take, for example, the case of water vapour, if the partial pressure of the water vapour were only the millionth of an atmosphere there would still be about 2.8×10^{13} molecules of water vapour per cubic centimetre. With such ionising agents as Röntgen rays, it is exceptionally strong ionisation when there are 10^{10} ions per cubic centimetre, so that even with the amount of water vapour mentioned above, which it would be very difficult to avoid, even with the most careful drying, there would be about 2800 times as many molecules as there are ions in an intensely ionised gas. In cases where there are an exceptionally large number of ions present as, for example, in the negative glow in a discharge tube, all kinds of chemical actions seem to go on with great facility.

We shall see later on how these polar molecules are able to bring about dissociation of salts in liquids as well as promote chemical action.

It can be shown [15] that if M is the electrostatic moment of a molecule, *i.e.*, the product of one of the charges into the distance between the charges in an electric doublet which would produce the same electrostatic effect as the polar molecule; then K, the specific inductive capacity of the gas at the absolute temperature T and at a constant density corresponding to that at 760 mm. pressure and 0° C., is given by the equations

$$K = a + \frac{.88M^2 \times 10^{36}}{T} \tag{26}$$

where a is independent of the temperature. Hence measurement of K at two different temperatures would give us M.

Applying this formula to the results of Bädeker's experiments, I find that for water

$$M = 2.1 \times 10^{-18} \tag{27}$$

for ammonia

$$M = 1.5 \times 10^{-18} \tag{28}$$

It is probable that determinations of K, and thereby of M, at different temperatures for different gases, would give us valuable information as to the lack of symmetry in the molecules of the gas.

ARRANGEMENT OF ELECTRONS IN OCTETS.

We have seen that when a shell of electrons surrounds a positive charge equal to the total charge on the electrons so that the system as a whole is electrically neutral, eight is the maximum number of electrons which can be in stable equilibrium on the shell. If some of the positive charge be taken from the inside of the shell and placed outside in symmetrical positions so as not to destroy the approach to sphericity of the shell of electrons, we can prove that though this transformation will increase the radius of the shell, it will not in general increase the stability, and that eight will still be the maximum number of electrons which can, consistent with stability, be on the shell.

Thus confining our attention to systems such as those formed by collections of atoms where there is no excess of one kind of electricity over the other, eight will be the maximum number of electrons that can be included on a single spherical surface, while, if there are less than eight, the system will not be saturated. It follows from this that any system of electrons and atoms which is stable and saturated must consist of a number of cells of electrons, each cell containing eight electrons and having a charged atom inside. It does not follow that all configurations which can be built up in this way are possible, for though each cell might be stable if all the electrons and positive charges outside it were fixed, yet an aggregate of such cells need not be stable if all the electrons and atoms can move quite freely. Thus we cannot be sure that all distribution of electrons into octets represents a possible compound—as a matter of fact, we know that many do not. Thus to take a system of octets like that shown in Fig. 17, which represents a line of cubes placed face to face, each cube containing a positive charge equal to four. This is an electrically neutral system, and corresponds to a long line of carbon atoms. This system turns out on mathematical investigation to be unstable and therefore a long chain of carbon atoms cannot exist, but would break up into shorter chains, each containing 2, 3 or 4 atoms; this is in accord with chemical experience. On the other hand, long chains of the radicle CH_2 exist in many organic compounds. I have found that the analogous system consisting of a row of doubly charged positive atoms, each of which is at the centre of a tetrahedron of electrons as in Fig. 18, is stable. Take, as another example, a long row of cubes placed edge to edge as in Fig. 19, each cube containing a positive charge 6, this would

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[15] *Phil. Mag.*, 27, p. 763 (1914).

FIG. 17.

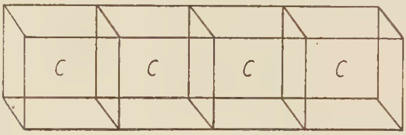
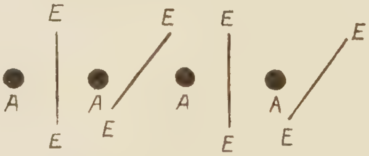


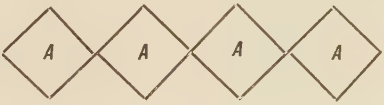
FIG. 18.



form an electrically neutral system and would correspond to a long chain of oxygen atoms. The mathematical theory, however, shows that this arrangement is unstable and this is confirmed by experience as compounds which contain even very short chains of oxygen atoms are highly explosive.

This division into octets may be regarded as a kind of entrance examination which every candidate for recognition as a formula representing the structure has to pass, and not as being necessarily either the right or even a possible formula. It is a necessary condition which every formula must fulfil, but it is not sufficient to ensure the stability of the compound. It was just the same on the old theory of valency; all kinds of compounds could be imagined which would satisfy the valency condition, but only a small fraction of these have been detected. In fact, chemistry is something more than freehand drawing.

FIG. 19.



If we wish to find any arrangement of octets which can represent a molecule consisting of specified atoms, we have to solve the following problem. The number of electrons at our disposal is known because we know the atoms of which the molecule consists; we know the number of cells because there is to be one round each of the atoms which in a free state have four or more electrons in the outer layer. Thus we know the number of cells required and the number of electrons at our disposal; we have to see if it is possible to arrange the electrons in octets. If the octets were separate and did not go shares in any electrons, each cell would require eight electrons. Whenever we make an octet share an edge with another, we save two electrons; if it shares a triangular face, we save three; if it shares a square face, we save four. We have to try to find contacts between the octets of such a kind that the saving of electrons will equal the difference between eight times the number of cells required and the number of electrons at our disposal. Thus to take an example, suppose we want the arrangement for two oxygen atoms; here two cells are required and there are twelve electrons at our disposal; we have therefore to save four electrons by the contact between the two cells; to do this the octets must have a square face in common, so that the only possible arrangement is that represented in Fig. 20.

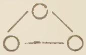
Suppose, however, we have three oxygen atoms to arrange in a molecule; hence we require three cells and we have eighteen electrons at our disposal; hence we have to save $3 \times 8 - 18 = 6$ electrons by the contacts. We may do this in two ways: In one represented in Fig. 21, we have three line contacts, at each of which two electrons are saved. In the other, we have that represented in Fig. 22, where we have one line contact, saving two, and a face contact saving four. The first arrangement is represented by , the second by $O=O-O$; which are two possible formulas for ozone. If both are possible, there must be two kinds of ozone; the first of these being quite symmetrical would represent a molecule without a resultant electric moment, the second we should expect to involve a finite moment.

FIG. 20.

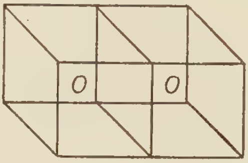
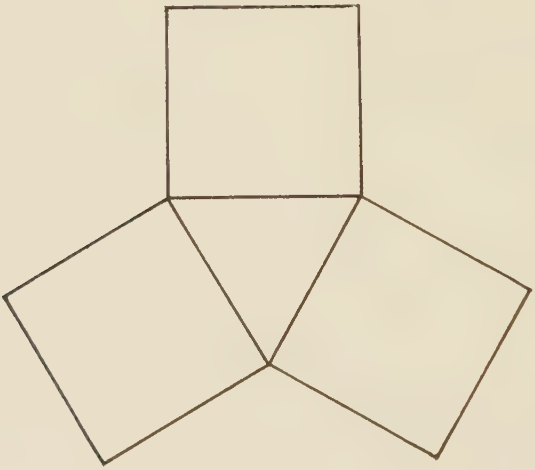


FIG. 21.



As we can detect the existence of electrostatic moments by experiment on specific inductive capacity, we may hope to find out whether or not there are two kinds of ozone and, if there is only one, which is the formula which represents its constitution.

For CO_2 we require three cells, and we have $4 + 2 \times 6 = 16$ electrons. We have, therefore, to save $3 \times 8 - 16 = 8$ electrons by the contacts; if the atoms are in a line there are only two of these, hence we have to save four at each contact, so that the configuration will be that represented in Fig. 23. This configuration can also be regarded as a quadruply charged carbon atom placed midway between two oxygen atoms surrounded by octets of electrons, each of these systems carrying a charge −2, the molecule being represented by $\underset{-2}{O}=\underset{4}{C}=\underset{-2}{O}$. We may point out that we might have another configuration for the same distribution of electric charges, *viz.*, that represented by Fig. 24; here the oxygen atoms carry the same charge as before, but they present an edge of the octet to the carbon atom instead of the full face. In this case we see that the layer of electrons nearest the carbon atom only contains four electrons, in that represented in Fig. 23 it contains eight. Thus this layer is saturated with the arrangement of Fig. 23, but not with that of Fig. 24. Thus if the

FIG. 22.

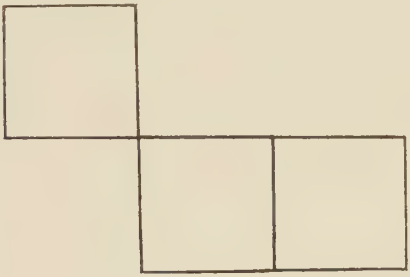
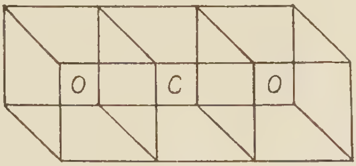
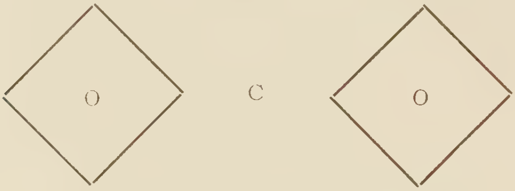


FIG. 23



electrons in CO_2 were arranged as in Fig. 24, the molecule would not be saturated; it could accommodate, for example, two molecules of water if these were arranged so that the water octet presented an edge to the carbon. While if they were arranged so that each of the water octets presented a point to the carbon atom instead of an edge, it could accommodate four molecules of water. If the oxygen atom also turned a corner to the carbon atom instead of an edge, there would be accommodation for six molecules of water. We thus see that where there are contacts such as those in Fig. 23, which are represented by double bonds between the atoms, we can, by altering the orientation of the cells, make room for other neutral molecules or radicles. The whole number of system nearest to the central atom must not, however, exceed eight.

FIG. 24.



DISPOSITION OF THE ELECTRONS IN TYPICAL COMPOUNDS.

This subject, as you are doubtless aware, has been treated very fully by Mr. Langmuir and Professor Lewis, starting from a different point of view from that adopted in these lectures. I shall therefore only discuss it very briefly.

Chlorides.—Monochlorides, type HCl. We have here a positive charge outside the octet. The compound has a finite electrostatic moment. The region around the hydrogen atom is comparatively free from electrons, thus negative ions or molecules of water could be held in stable equilibrium round the hydrogen ion, so that substances with this composition should be hygroscopic.

Bichlorides, type $CaCl_2$. A double positive charge between two octets; the molecule is non-polar. If each of the octets presents a face to the calcium atom, there will be eight electrons on a sphere round this atom; with this configuration there is no room for other molecules. If the chlorine octets swing round so as to present an edge instead of a face to the calcium atom, there will only be four electrons on the layer next to this atom. Thus there would be room for two water molecules if the water octets came edge foremost, or for four if they came point foremost. While if the chlorine octets were also point foremost to the calcium atom, there would be room for six molecules of water. We should expect these chlorides to be very hygroscopic.

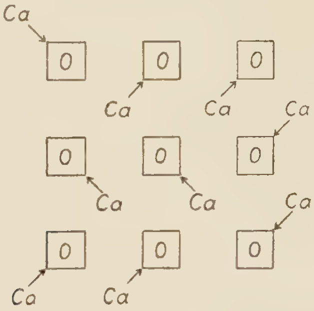
An interesting fact about the halides is that we find chlorides such as tungsten hexachloride, WCl_6, and molybdenum pentachloride, $MoCl_5$, sulphur hexafluoride, SF_6, in which there are more than four atoms of chlorine or fluorine combined with one atom of another element. Now if each octet is to present an edge to the central atom, it will furnish two electrons to the layer round the central atom and as the number of electrons in this layer cannot exceed eight, it follows that there cannot be more than four atoms of one kind combined with one of another, a rule to which there are a few exceptions, such as these we are considering. We may explain the existence of these in two ways—one is to suppose that only four of the chlorine atoms are in the inner zone, that the other two are in the outer zone. In this case two chlorine octets carrying a negative charge would be easily detached, so that the compound should be a good electrolyte. The other supposition is that all the chlorine octets are in the inner zone, but only two of them present an edge to the central atom, the other four only presenting a corner. The difference between the two is roughly that on the first supposition, two chlorine octets are loosely and four firmly held, while on the second two are firmly and four loosely held.

Oxides.—The points previously raised in connection with water apply to the oxides of the univalent elements generally.

Oxides of divalent elements of the type CaO. Here we have the core of the calcium atom outside the oxygen octet. If this octet presents an edge towards the calcium atom, there will be room for three more octets, each presenting an edge, so that we can easily understand why this substance dissolves easily in water. It is not necessary that the octets which go to complete the tale round the calcium atom should be those of water molecules, they may be the octets of other CaO molecules. The fact that the octet of one molecule of CaO can also find its way into the inner zone surrounding other Ca atoms, will have a great effect in binding the different molecules together and thereby account for the very high melting points of the oxides. The arrangement in two dimensions when molecules of CaO mutually saturate each other is shown in Fig. 25. The arrow between Ca and O indicates that two electrons have gone from this particular calcium atom to complete the octet round the oxygen atom. The octets are supposed to present their edges to the calcium atom.

Sesquioxides, type B_2O_3. The most symmetrical arrangement for oxides of this type would seem to be one where the three oxygen octets have their centres at the corners of an equivalent triangle, while the cores of the two boron atoms are symmetrically placed on an axis at right angles to this triangle and passing through its centre.

FIG. 25.



Carbonates.—M_2CO_3. We have here three oxygen octets surrounding a central carbon atom. If the inner zone round this atom is to be saturated with electrons, one of the octets must turn a face, while the other two octets present edges, towards the carbon atom. If the octet turning its face to the carbon twists round and turns an edge, there will be room for another octet in the inner zone; thus the molecule can take up water or bind itself to other molecules of the carbonate. There would seem to be the possibility of two isomers, in one both the metal atoms are attached to the octets which present edges to the carbon; in the other, one metal atom is attached to the octet presenting a face and the other to one of those presenting an edge.

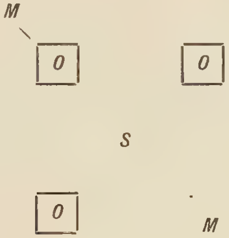
Nitrates.—MNO_3. The arrangement is the same as for the carbonates, except that the central atom is nitrogen, with a positive charge of five and not carbon with a charge of four, and there is only one metal atom instead of two to put outside the octets. There is the possibility of two isomers as before.

Sulphates.—M_2SO_4. Here we have four oxygen octets surrounding a central sulphur atom. These must have edges and not faces turned towards this atom. As all the four octets are turned the same way and are similar there will be no isomers.

Perchlorates.—$MClO_4$. The same as the preceding, except that the central atom is chlorine and not sulphur, and there is only one metal atom to place outside the octets.

Sulphites.—M_2SO_3. These from our point of view differ from the carbonates and nitrates because after providing for the electrons to furnish the three oxygen octets, there are still two electrons to provide for. The most symmetrical way would be to arrange them as in Fig. 26, *i.e.,* with one of the M atoms connected directly up with the sulphur and not indirectly through an oxygen octet. This would put the metal atom in the inner zone, from which we should not expect it to be detached in electrolysis; thus if M were hydrogen, this arrangement would correspond to a monobasic acid. H_2SO_3 is, however, dibasic and therefore has probably both the H atoms connected directly with the oxygen and not with the sulphur. In this case we see that there are two electrons which have no direct connection with any but the sulphur atom, and which would be available for attaching to the M_2SO_3 molecule the positive part of any polar molecule or to complete the octet of an oxygen atom and thus form the sulphate.

FIG. 26.



Chlorates.—$MClO_3$. Here we have the same number of electrons as in the sulphites, but the fact that the chlorates very readily give up oxygen while the sulphites take it up, suggests a different grouping of the electrons. The arrangement given in Fig. 27, where one of the oxygen atoms is bound to another oxygen atom and not directly to the chlorine, would represent a molecule which would readily part with oxygen.

This arrangement of two oxygen octets with an edge in common is one that occurs in connection with the molecules of exceptionally intense oxidising agents, and we have already met with it when considering the form of the molecule of ozone. In hydrogen peroxide H_2O_2 there are two possible forms, one represented by Fig. 28: (*a*) In which both hydrogen atoms are attached to the same oxygen octet, and the other (*b*) when one hydrogen atom is attached to one oxygen octet and the other to the other. In both cases we have two oxygen octets connected together by an edge. The first one would possess a finite electrical moment, the second one would not, so that the forms could be distinguished by measuring the specific capacity of H_2O_2 in the gaseous state.

FIG. 27.

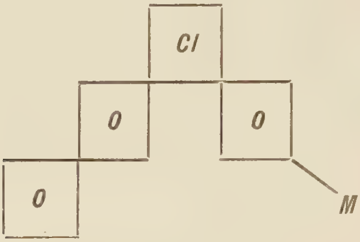
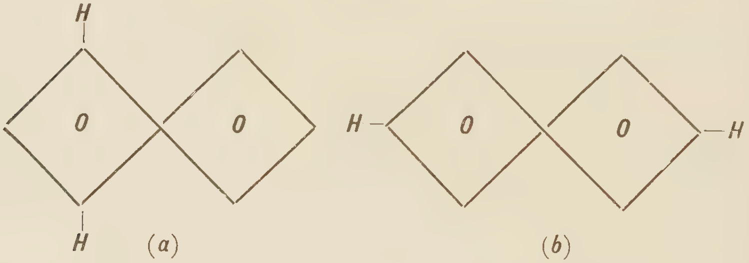


FIG. 28.



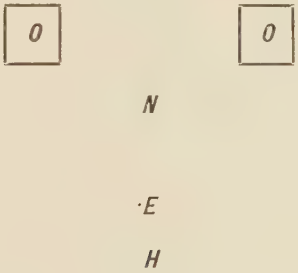
(*a*) (*b*)

Nitrites.—HNO_2. The nitrites resemble the sulphites in having two electrons which are not in direct connection with any but the central atom. There are two oxygen octets and two electrons *E*, as in Fig. 29. If the hydrogen ion took up the position (H), it would be bound by these electrons, the hydrogen would be in the first zone and the substance would not be an acid. If the hydrogen is attached to one of the oxygen octets, the substance will be an acid, and the two electrons will be free to complete the octet round a neutral atom of oxygen, link it up with the nitrogen, and convert the nitrite into a nitrate.

CONNECTION BETWEEN CHEMICAL CONSTITUTION AND CHEMICAL PROPERTIES.

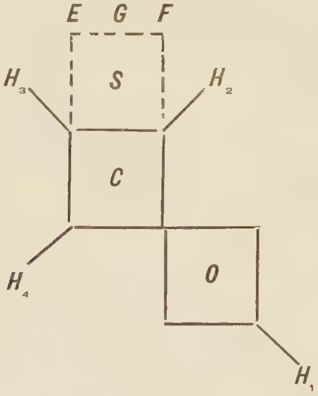
If we know the distribution of the electrons and positive charges in a molecule, the behaviour of the molecule under specified physical conditions can be calculated from the forces exerted on each other by the electric charges. The exact calculation in most cases would be a process of considerable length, but we can get without an appreciable amount of mathematics a general idea of the nature of the change in properties likely to be produced by changes in the composition of the molecule. The clearest way of illustrating the point in question is to take an example. Methyl alcohol CH_3OH is a substance without any tinge of acid properties; in fact, it is basic, if anything. When, however, two of the hydrogen atoms are replaced by an oxygen one we get formic acid, a substance with pronounced acid properties. We know the general character of the distribution of electrons in the two cases, can we see why the difference in the distribution should make the difference between an acid and a feeble base? We shall suppose that the acid character of a substance containing the hydroxyl radicle OH depends on the ease with

FIG. 29.



which the hydrogen ion H can be detached from the oxygen. We have therefore to see what is the difference between the force on the hydrogen ion in CH_3OH and CH.O.OH. The arrangement of the electrons in methyl alcohol is represented in a general way by the continuous lines in Fig. 30, where for the sake of avoiding confusion in the drawing, the tetrahedral arrangement of the H_3, OH atoms round the central carbon atom has been replaced by an arrangement in one plane. We have the octet round the carbon atom; the size of this does not vary much from one compound to another. We may thus regard this octet as occupying much the same position in the formic acid as in the methyl alcohol. Consider the difference when we replace two of the hydrogens H_2, H_3 by an atom of oxygen. We take away the positive charges H_2H_3, and replace them by a positive charge 6 at the centre *S* of the oxygen octet, and four negative electrons at the corners *E,F* of the face of this octet. Thus the difference between the forces on the atom H_1 in the hydroxyl radicle in the methyl alcohol and formic acid is the difference between the force exerted by the positive charge 6 at *S*, by the four electrons on the face *EF* of the octet, and that exerted by the two positive charges H_2H_3, which can be represented approximately by a positive charge 2 at *S*. Subtracting this from the charge 6 due to the oxygen, we see that the change due to substituting the oxygen for the two hydrogens can, as far as the forces are concerned, be represented by a plus charge 4 at *S*, and a charge on the whole amounting to −4 carried

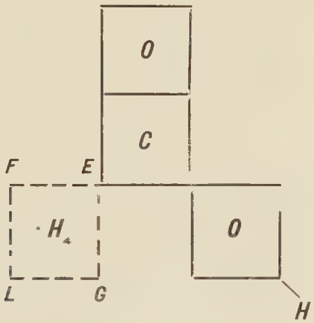
FIG. 30.



by four electrons at the corners of the square face of the octet. If we replace these by a charge –4 at *G*, the centre of the square face, then the force on H_1 in the formic acid molecule will equal the force on H_1 in the molecule of methyl alcohol plus the force due to the doublet with a positive charge 4 at *S* and a negative one –4 at *G*. The effect of the doublet is, as will be seen from the figure, to repel H_1 away from O. It will thus tend to detach H_1 from the molecule, *i.e.*, to make the molecule act like an acid.

As a further example let us consider whether replacing a hydrogen atom in such a compound as formic acid by a chlorine one would increase or diminish the acid properties of the molecule.

FIG. 31.



Suppose that Fig. 31 represents the distribution of the electrons in a molecule of formic acid. If the hydrogen H_4 were replaced by chlorine, the change as far as the electrical forces are concerned will be that the charge +1 at H_4 will be replaced by a charge +7 carried by the chlorine atom, and that six other electrons will be introduced which, with the two along the edge *E*, will make up the octet round the chlorine atom. To calculate the effect of these six electrons, we take the four along the edges *F* and *G;* these are at the corners of a rectangle whose centre is at *S*, the centre of the chlorine atom. If these electrons act as if they were concentrated at the centre of figure *S*, they will have the effect of reducing the positive charge at the centre of the chlorine atom from 7 to 3. Now take the two electrons at the edge *L;* these with two of the three charges at the centre of the chlorine atom will form an electrical doublet whose moment is $2e \times LS$ with its positive part turned towards the centre of the molecule, the remaining positive charge at *S* will represent the positive charge on the hydrogen atom before it was replaced by chlorine. Thus the difference in the forces due to the replacement of hydrogen by chlorine is represented by the electrical doublet $2e.LS$, and this as we see from the figure will tend to drive off the hydrogen in the hydroxyl radicle—thus the substitution of chlorine for hydrogen tends to increase the acidity of the molecule. This is very strikingly shown by monochlor, dichlor and trichlor acetic acids, which are much stronger acids than acetic acid itself.

It follows from the investigation we have just given that if in a hydrocarbon such as CH_4 we substitute for one of the hydrogen atoms E, the atom of an electronegative element such as chlorine, the change in the electric forces can be represented by the introduction of an electrostatic doublet at E with its axis along CE and the positive part of the doublet turned towards C. The molecule of CH_4 before the substitution of the chlorine atom was non-polar, *i.e.,* the molecule had no electrostatic moment, the substitution of the chlorine for the hydrogen introduces a finite electrostatic moment and thus makes the molecule polar.

The positive part of the doublet at E is turned towards C, hence the force it produces at F, G, H, the other corners of the tetrahedron whose centre is at the carbon atom, will tend to attract negatively and repel positively charged atoms. Hence if a molecule of CH_3Cl were placed under such conditions that there were positively and negatively charged atoms in its neighbourhood, the concentration of the negative atoms round F, G, H would be greater than it would be for the molecule CH_4 before the hydrogen at E had been replaced by the electronegative chlorine. Thus the substitution of the atom of an electronegative element for one of the hydrogen atoms round the carbon will tend to promote the substitution of electronegative atoms for the remaining hydrogen atoms. If two of the hydrogen atoms are replaced by an atom of oxygen, this will for the same reason promote the substitution of electronegative atoms for the other two hydrogen atoms. We have illustrations of this effect in the following examples for which I am indebted to Mr. W. H. Mills.

Ethyl chloride + chlorine (1 molecule) in the liquid state under the influence of ultra-violet light,

$$CH_3\,.\,CH_2Cl \longrightarrow \underset{\text{70 per cent.}}{CH_3\,.\,CHCl_2} + \underset{\text{10 per cent.}}{CH_2Cl\,.\,CH_2Cl}$$

Ethyl bromide heated with bromine in sealed tube,

$$CH_3 . CH_2Br \longrightarrow CH_3 . CHBr_2$$

Chlorine on boiling toluene ($C_6H_5.CH_3$) in sunlight gives successively

$$C_6H_5CH_2Cl, \; C_6H_5CHCl_2, \; C_6H_5CCl_3$$

We see from these examples that there is a tendency for a new hydrogen atom to go into that part of the molecule which is already halogenated.

In the presence of catalysts such as ferric bromide, the halogen atoms in the higher members of the series go to the carbon atom adjacent to the one already brominated.

Another illustration of this effect is the well-known fact that when an organic compound is oxidised the carbon atom attacked is the one which already is attached to oxygen.

I pass on now to consider a problem which I can best explain by stating a particular case. Why is it that in a compound such as methyl alcohol $H_3C.OH$ the only atom of hydrogen which is replaceable by a monovalent metal is the one in the hydroxyl radicle. Or to take another aspect of the same problem, why can the hydrogens in marsh gas not be replaced by the monovalent positive elements, while they can be replaced by the monovalent negative ones like Cl, Br, I? Let us consider what are the conditions for the existence of CH_4. We have an octet of electrons round the carbon atoms. The carbon atom which only carries a charge of four units could not by itself keep eight electrons in stable equilibrium. It is enabled to do this by the stabilising effect of the positive charges which are on the hydrogen atoms. This stabilising effect will depend on the distance of the positive charge on the hydrogen from the nearest electron in the octet, a distance which we should expect to be not greatly different from the radius of the hydrogen atom. Consider now the effect of replacing the hydrogen atom by one of an alkali metal; the radius of the atom of the alkali metal is very considerably greater than that of the hydrogen atom. The control over the electron in the metal is much less than that on the electron in the hydrogen atom. This is shown by the fact that the ionising potential for the hydrogen atom is much greater than that for the metal one, thus we should expect the stabilising effect of the positive part of the metal atom to be very considerably less than that of the hydrogen atom. Thus while the stabilising effect of the hydrogen atom may be great enough to make the octet of electrons round the carbon atom stable, that of the metal atom may not be able to do so, in which case the metallic compound could not exist.

In this view the atoms of the monovalent metals are not efficient stabilisers of an octet of electrons, and we should expect that in the compounds they form the octet should be of a kind that requires little help from the positive charge on the metal atom to make it stable.

Let us consider a few types of the salts formed by these monovalent metals. Let us begin with the chlorides, here we have an octet of electrons round the chlorine atom and the positive charge outside. Now experiments with positive rays show that a neutral chlorine atom, having seven electrons in the outer layer readily takes up a negative charge, *i.e.,* acquires another electron. Thus an octet of electrons round a chlorine atom is stable even without the assistance of an external positive charge, and thus a metal atom outside an octet round a chlorine atom will be a system where the octet is very stable. Hence we should expect that all these alkali metals would, as in fact they do, form chlorides readily. Now let us turn to the hydroxides. The neutral hydroxyl radicle has seven electrons arranged round the oxygen atom. Now again experiments with positive rays show that the hydroxyl radicle very often occurs with a negative charge and in this state there must be an octet of electrons round the oxygen atom. Thus such an octet with the hydrogen atom outside is stable by itself even without assistance from the positive part of a metallic atom. Thus when it gets this assistance the octet will be very stable, so that we should expect, as in fact is the case, that the hydroxides of the alkali metals would be formed very readily.

Now let us turn to the oxides, here we have an octet round the oxygen atom and the positive part of two metallic atoms outside. As lines corresponding to negatively electrified oxygen atoms are to be seen on nearly every positive-ray photograph, a system of seven electrons round the oxygen atom must be a stable system In the case of the metallic oxides we have two positive charges to make the system stable when another electron is added. We have seen from the case of hydroxyl that a single hydrogen atom is able to bring about this stability, so that as two metal atoms are available the metal atoms would have to be very inferior to the hydrogen one as stabilisers if the octet were not fairly stable.

Now let us consider why it is that, while we cannot replace by a metal one of the hydrogen atoms directly connected with the carbon atom in a hydrocarbon, we can replace the hydrogen in a hydroxyl group linked up to the carbon. Let us take methyl alcohol as an example, where we may suppose the electrons are arranged as in diagram 30. We see that from its position the hydrogen in the hydroxyl group has little to do with the stability of the octet round the carbon atom; it is the stability of that round the oxygen atom with which it is concerned. Now an octet round an oxygen atom is a very different thing as far as stability is concerned from one round a carbon atom. We have seen that seven electrons can be in stable equilibrium round an oxygen atom without any help from systems outside and that a single positively charged hydrogen atom outside is sufficient to make the octet stable. If the hydrogen in the hydroxyl is replaced by a metallic atom, then to keep the octet round the oxygen atom stable we have not only the positive part of the atom of the metal, but also that of the carbon atom with its attached electrons and positive hydrogen atoms. Thus the conditions are much more favourable for the stability of this octet than they are for that round the carbon atom, and thus it may be possible to replace the hydrogen in the hydroxyl but not that in the rest of the atom. The positive rays afford evidence that to make the octet of electrons round the carbon stable in a compound CH_3X, where X is a monovalent element, assistance is required from X. For if it were not, the system got by removing the positive part of X would be stable, but this system is just the radicle CH_3 with a negative charge. Now the line corresponding to this radicle occurs frequently in positive rays, but always with a positive charge, while other radicles, such as OH, are found with negative as well as with positive charges. This is an indication that the stability of the octet round the carbon atom depends upon the presence of X. On the other hand, if the residue after taking away an atom of hydrogen from a hydrocarbon is stable even after receiving a negative charge we should expect that the hydrogen atom might be replaced by an atom of the metal, for the molecule is stable after the hydrogen has been removed and the octet does not depend on the positive charge for its stability. Now on many positive-ray photographs I have observed a line corresponding to a molecule with a negative charge, whose molecular weight is 25, when hydrocarbons were in the discharge tube. The molecular weight indicates that the molecule is C_2H, *i.e.*, acetylene minus an atom of hydrogen, if this is so the hydrogen in acetylene might be replaced by a metal: The compound C_2Cu_2 which is of this type is well known.

Though we have seen the stability of the oxides indicates that the octet round the oxygen atom can be stabilised by the presence outside it of the positive parts of metallic atoms, there are indications that this octet is not so stable as those in the chlorides and hydroxides. The main evidence is that many oxides and sulphides when in the solid state are conductors of electricity, especially at high temperatures, and that, as the researches of Königsberger and Horton show, this conductivity is not electrolytic, but resembles that through metals. There are some chlorides which conduct in the solid state, but as far as I am aware their conductivity is always electrolytic. The conductivity of metals can, as we shall see, be explained as due to electrons which move freely about in certain directions through the solid. So that the non-electrolytic conductivity of these oxides and sulphides indicates that some electrons have got free, *i.e.*, that some of the octets round the oxygen and sulphur atoms have broken up. This breaking up increases very rapidly with the temperature. Another piece of evidence to the same effect is the very intense thermionic emission by oxides such as those of calcium, strontium and barium, an emission which, as Horton has shown, is far more intense than that from the metals themselves at the same temperature. On our view this is due to the breaking up of the octets round the oxygen atoms. The smaller the charge on the neutral atom, the more will the stability of the octet round it depend on the positive charges outside. Thus as nitrogen has only a charge 5 while oxygen has one of 6, we should expect the octet round nitrogen in a metallic compound to be more easily broken up than that round oxygen in metallic oxides and that the non-electrolytic conductivity should be greater. It would be interesting to test from this point of view the properties of tripotassiumamide, NK^3.

CHAPTER III.

RESIDUAL AFFINITY, MOLECULAR COMPOUNDS, WERNERS COÖRDINATION NUMBERS.

We have regarded the molecule of a chemical compound as made up of atoms some of which have lost electrons, while others have gained them, so that the former are positively, the latter negatively, electrified; the forces between the electrical charges on the atoms and electrons binding the atoms together in such a way as to form a stable system. The number of electrons which an atom can gain or lose depends upon the nature of the atom. The number it can lose is equal to the number of electrons in the outer layer, and varies from one to eight according as the element belongs to one or other of the Mendeleefian groups; the number it can receive is 8 minus the number in the outer layer.

If the transference of electrons has proceeded to its limit, *i.e.*, if every positively charged atom has received the maximum positive charge of electricity it can acquire and every negatively charged one its maximum charge of negative electricity, there must be simple relations between the number of different kinds of atoms in a neutral molecule. Thus, for example, if we have two kinds of atoms, *e.g.*, calcium and chlorine, since the neutral calcium atom has two electrons in its outer layer and the neutral chloride seven, the calcium atom can lose two electrons while the chlorine atom can only gain one. We see therefore that when the transference of electrons has gone as far as possible, each calcium atom will have given up its electrons to two chlorine atoms neither more or less and thus for each calcium atom positively charged there must be two chlorine ones with negative charges, thus the composition of the molecule would be represented by the symbol $CaCl_2$. And we can show easily that when the transference of electrons has proceeded to the limit the proportion between the numbers of the various kinds of atoms in the molecule will be the same as that deduced from the ordinary principles of valency.

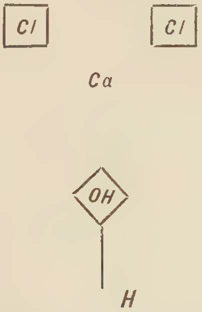
In such a molecule as $CaCl_2$ the transference of electrons has reached its limit, and as far as this property is concerned the molecule may be regarded as "saturated." Unfortunately there has been a tendency to regard this "saturation" as applying to quite a different thing. Some chemists have supposed not merely that the calcium atom when it had charged two chlorine atoms had exhausted its power of charging up any more atoms negatively, which is true, but they implied, which is not true, that the doubly charged calcium atom cannot by its attraction hold more than two atoms in stable equilibrium. It is important to distinguish between the maximum positive charge the atom can acquire and the maximum number of negatively electrified systems which the maximum charge can hold in stable equilibrium in a single layer around it. The table given in the first chapter shows that when the attractive force between the positive charge and a negative one is represented by $\frac{a}{r^2} - \frac{b}{r^n}$, the number of negative charges which a positive charge can hold in stable equilibrium in a single layer is, when the positive charge does not exceed a limit determined by the value of n, greater than the number of units of positive charge on the central system. This is confirmed by the fact that the positive-ray method reveals the existence of negatively charged atoms, for example, the atoms of hydrogen, carbon, oxygen, chlorine are frequently found to be negatively charged, and a negatively charged atom must have more electrons than the number of units of positive charge. Thus, though a calcium atom could not itself charge negatively more than two chlorine atoms, yet if a third chlorine atom, negatively electrified by some external agent, were brought near the calcium atom, it would hold it in stable equilibrium and form the system $\underset{+2}{\mathrm{Ca}}\ \underset{-}{\mathrm{Cl}}\ \underset{-}{\mathrm{Cl}}\ \underset{-}{\mathrm{Cl}}$. This system would, however, be negatively charged and so could not be expected to remain free under normal conditions; it might, however, be found in electrolytes or charged gases. There may, however, be electrically neutral compounds in which the calcium atom is surrounded by more than two systems. Let us suppose that instead of bringing up a negatively electrified chlorine atom to the $CaCl_2$, we bring up a molecule which possesses considerable electrical moment, *i.e.*, one in which the positive and negative parts are separated by a considerable distance, such, for example, as a molecule of water $\underset{+}{\mathrm{H}}\underset{-}{(\mathrm{OH})}$. The negative end of this would place itself closer to the calcium than the positive one and we should get a system such as that represented in Fig. 32.

This system as a whole is electrically neutral and so could exist under normal conditions; it would be held together by forces of just the same type as those which hold the atoms together in $CaCl_2$, yet from the ordinary chemical point of view the latter is a valency compound while the former is not.

It must be noticed, however, that though the number of systems that can exist round the central atom may be greater than the positive charge on that atom, theory indicates that there is a sharp limit to this number, so that the possible compounds of this type would be determined by definite rules.

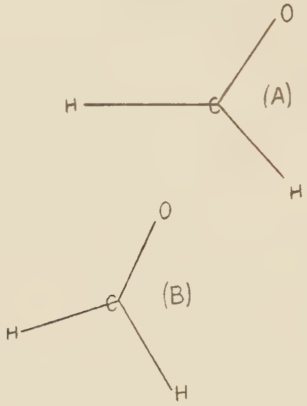
We can get some information about the number of atoms or molecules which can be grouped in stable equilibrium about a central system *S* by applying the condition for stability which we have already used when considering the stability of arrangements of electrons in the atom. Let us suppose that the atoms grouped around *S* are the centres of octets of electrons, the electrons in these octets which are nearest to *S* will furnish a layer of electrons round *S* and for stability the number of electrons in this layer must not exceed eight. The number of electrons an octet will supply to this layer will depend upon the orientation of the octet. If *O* is the centre of the octet, then if *SO* passes through an electron, *i.e.*, if the octet presents a corner to *S*, it will supply one electron to this layer. If *SO* bisects at right angles the line joining two electrons on the octet, *i.e.*, if the octet presents an edge to *S*, two electrons will be supplied, while if *SO* is at right angles to a face of the octet, *i.e.*, if the octet presents a face to *S*, four electrons will be supplied. When all the octets present corners to *S* the maximum number around *S* will be eight. Considering the exiguous character of this connection between *S* and the octets,

FIG. 32.



we should not expect this arrangement to have any very great stability. If each octet presents an edge to *S*, the maximum number of octets will be four, while if each presents a face to *S*, the maximum number will be two. Thus the number of systems which can be held in stable equilibrium in the first zone round *S*, which following Werner we shall call the coördination number of *S*, may vary from 2 to 8. Werner finds that an appreciable number of elements have a maximum coördination number four, a few have eight, the number for the majority is, however, six, which would correspond to four of the octets presenting a corner, and two an edge to *S*.

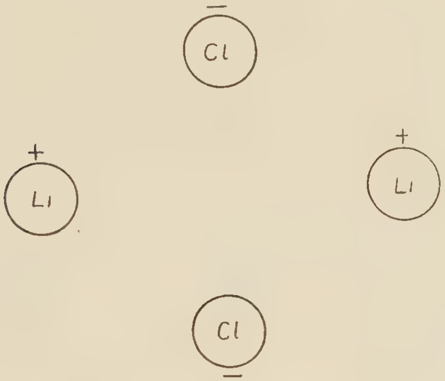
FIG. 33.



The coördination number is never less than the valency and is generally greater. The somewhat vague notion implied by the use of the term "Residual Affinity," which appears frequently in chemical literature, is an attempt to give expression to the facts implied by a difference between the valency and the coördination number. The consequences of this difference are of the first importance. Let us see, for example, how it would facilitate the aggregation of molecules. Let us take as an example formaldehyde COH_2, a substance which is saturated for valency purposes, but is not coördinately saturated. Thus if *A* (Fig. 33) represents a molecule of formaldehyde, then if the coördination number of carbon is four, *A* can hold another negatively electrified oxygen atom in its shell; this may form a part of another formaldehyde molecule *B*, and thus *A* and *B* may be held together in the way indicated in Fig. 33. As *B* is not coördinately satisfied, it may link up with the oxygen from a third molecule *C;* in this way aggregates of the formaldehyde molecule would be formed readily.

We can apply to the union of molecules considerations quite analogous to those we applied to the combination of atoms. Thus, for example, we can picture two molecules of Li Cl joined together by an arrangement like Fig. 34, which is similar to that binding two atoms of lithium together, the electrons in the latter being replaced by negatively electrified atoms in the chloride. Indeed,

FIG. 34.



if the coördination number were always eight, the molecular compounds would run quite parallel with the atomic ones, *e.g.*, the atoms would be arranged in octets in the molecular compounds just as the electrons are arranged in octets in the atomic ones. Since eight is the maximum number of electrons which can be arranged in one layer round a central atom, eight is the coördination number of an atom with respect to electrons; hence when the coördination number in molecular compounds is eight, we see that the molecular compounds will run parallel to the atomic ones. Let us apply this result to a particular case. We saw that when the atoms of an element contain few electrons, so few that these are not sufficient in a diatomic molecule to make up the total of eight, the molecules have a great attraction for each other, so that the element under normal conditions is in the solid state, *e.g.*, Li, Be, Bo, C. When, however, there are sufficient electrons in the atom for the atoms in a diatomic molecule to make up, by sharing electrons, one or more octets, the molecules have but little attraction for each other, and the element is gaseous, *e.g.*,

N_2, O_2, F_2, Ne. Considerations of exactly the same character will apply to the molecular compounds formed, for example, by the chlorides. A chloride like NaCl, which contains only one chlorine atom, is analogous to an atom containing only one electron; a chloride like $BeCl_2$, which contains two chlorine atoms, to an atom containing two electrons and so on. The molecules formed by atoms which contain less than five electrons exert great attractions on each other and condense into the solid state, while those containing five or more electrons are much more volatile and for the elements in the first period are gaseous. The result we have just obtained shows that we may apply to the chlorides the same reasoning as we applied to the atoms. Hence we should expect those chlorides which contain only a small number of chlorine atoms, to be solids; while those containing more than a certain number of chlorine atoms should be much more volatile. The following table of the boiling points of the different chlorides and fluorides shows that this is the case to a very marked extent.

The number of halogen atoms corresponding to a volatile or non-volatile substance will depend upon the coördination number of the element with which the halogen atoms are combined. The smaller the coördination number of the element, the smaller the number of chlorine atoms required to make the chloride volatile. As the coördination number varies from element to element, the connection between volatility and the number of chlorine atoms cannot be expected to be as clear cut as that between the volatility of an element and the number of electrons in the atom, as the coördination number of an atom with respect to an electron is always eight. The non-volatility of some of the chlorides such as WCl_5, WCl_6 is, I think, due to the chlorine atoms being in two layers, so that the number in the outer layer, which determines the volatility, is less than the number of chlorine atoms in the compound.

Another example of the analogy in physical properties for similar proportions between the number of electrons in the atom and the number of chlorine atoms in a chloride is afforded by the consideration of the electrical properties of the elements and of chemical compounds.

When there are less than four electrons in the outer layer of an atom of an element, the element is a metal and a good conductor of electricity, the conductivity arising from the movement

Compounds Containing One Halogen Atom.

Name.	Formula.	Melting point.	Boiling point.
Sodium chloride	$NaCl$	776	
Silver chloride	$AgCl$	450	
Sodium fluoride	NaF	above 902	

Compounds Containing Two Halogen Atoms.

Calcium chloride	$CaCl_2$	720	
Magnesium chloride	$MgCl_2$	708	
Strontium fluoride	SrF_2	above 902	
Calcium fluoride	CaF_2	above 902	
Stannous chloride	$SnCl_2$	250	620

Compounds Containing Three Halogen Atoms.

Antimony trichloride	$SbCl_3$	73	223
Bismuth trichloride	$BcCl_3$	230	430
Boron trichloride	BCl_3	liquid	18

Compounds Containing Four Halogen Atoms.

Silicon tetrachloride	$SiCl_4$	liquid	50
Stannic chloride	$SnCl_4$	liquid	114
Titanium tetrachloride	$TiCl_4$	liquid	135
Silicon tetrafluoride	SiF_4	gas	

Compounds Containing Five Halogen Atoms.

Antimony pentachloride	$SbCl_5$	gas	
Molybdenum pentachloride	$MoCl_5$	194	268
Tungsten pentachloride	WCl_5	248	278

Compounds Containing Six Halogen Atoms.

Sulphur hexafluoride	SF_6	gas	
Tungsten hexachloride	WCl_6	275	346

of the electrons: when there are more than four electrons in the outer layer the element is a bad conductor of electricity. The electrical conductivity of fused chlorides may be compared with that of the metals, the negatively electrified chlorine atoms taking the place of the electrons and making the conduction electrolytic. Chlorides containing a small number of chlorine atoms are good conductors when fused, while the higher chlorides like $SnCl_4$, CCl_4 insulate, although they are in the liquid state.

The thermionic properties of metals find, too, a parallel in those of the chlorides. A metal contains lattices of positively electrified atoms and electrons, the solid chlorides, lattices of the atoms of the metal and of negatively electrified chlorine atoms, and the work required to eject a chlorine atom from the salt would be of the same order as that required to eject an electron from the metal. Again, the proportion between the number of atoms and electrons in the metal would be the same as that between the number of metal atoms and of chlorine atoms in its chloride. Hence we should expect from thermodynamic considerations that at temperatures at which the thermionic emission of electrons from the metal is considerable, there should be an emission of negatively electrified chlorine atoms from the salt. Such an emission does in fact take place.[16] When salts are first heated considerable currents are carried by the chlorine atoms and no electrons can be detected. The effects produced by prolonged heating are very complicated, more so even than those occurring on the emission of electrons from hot metals. This is what we might expect, as the tearing away of the chlorine atoms would produce a more fundamental change in the surface than the emission of electrons from a metal. After prolonged heating electrons, as well as chlorine atoms, are given off, suggesting that the tearing away of the chlorine atoms has produced an excess of metal atoms at the surface.

When the coördination numbers of the metals occurring in double salts are not all equal, the arrangement of the electronegative atoms round the atom of the metal will not be in octets, but one which provides a layer of negative atoms round each atom equal to the coördination number of that atom.

Before leaving the consideration of the coördination number we must raise the question whether a doubly charged atom like oxygen ought to count as two towards the coördination number as it does towards the valency. If we take the view before discussed, the oxygen atom for coördination purposes ought to count as one and not as two. On that view the limits to the coördination number depend on the octets round the central atom. An octet with a double charge, such as that associated with an oxygen ion, can be orientated so as not to bring more electrons into the layer next the central atom than an octet with a single charge like that associated with a chlorine ion, thus the oxygen need not count for more than the chlorine.

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[16] Richardson, "Emission of Electricity from Hot Bodies."

ELECTROLYTIC DISSOCIATION.

When the coördination number of the central atom is greater than its valency, the molecule can combine with polar molecules such as H_2O, NH_3 to form new compounds in which the atoms in the original molecule are driven further apart, and are therefore able to rearrange themselves with the expenditure of much less energy than would have been necessary if these compounds had not been formed. Positively and negatively charged atoms may in this way be thrust so far apart and the connection between them made so slight that they move in opposite directions under the action of an electric field, and are thus resolved into ions.

This is well illustrated by the well-known example given by Werner of the ammoniates of platinic chloride. If the coördination number of platinum is six, then in $PtCl_4$ there is room for two polar molecules in the first layer round the platinum atom without that layer becoming unstable. The chlorine atoms are in direct connection with a platinum atom and so cannot be detached easily from it. Thus the compound $PtCl_4(NH_3)_2$ is not an electrolyte. If, however, more molecules of NH_3 are added, since 6 is the maximum number of constituents which can be in one layer round the positive charge, the constituents in the inner layer must break up into two groups, one group forming a layer of six next the platinum, the remainder forming an outer layer at some distance from the inner one. The process is very closely analogous to that described in Chapter I when new layers of electrons are formed when the number of electrons in the atom exceeds the number which can be held in stable equilibrium in one layer by the central positive charge.

Thus if four molecules of ammonia are added to the platinic chloride, there must be two constituents in the outer layer; if these are chlorine atoms carrying a negative charge they will be easily detached and form negative chlorine atoms and the compound will be, as Werner showed it is, an electrolyte, with ions $\underset{+}{PtCl_2(NH_3)_2}$ and $\underset{-}{Cl}\ \underset{-}{Cl}$. The work required to separate the ions comes from the loss of potential energy due to the approach of the polar molecules to the central system, and not from thermal agitation. The reasons in favour of this view of electrolytic dissociation are in my opinion very strong. I have already pointed out that to ionise a molecule isolated from other molecules would require an amount of energy comparable with the "ionising potential" of one of its atoms, a quantity varying from one element to another, but comparable with 10 volts. As the average kinetic energy of a molecule at 0° C. due to thermal agitation is, when measured on the same scale, only about 1/30 of a volt, it will be seen that there is little likelihood of the ionisation being due to thermal agitation.

On this view of electrolytic dissociation the ions in the solution are not simple atoms or radicles, but combinations of these with polar molecules. These molecules not only dissociate the original molecule, but after dissociation they tend to keep the ions apart. They surround the charge on the central atom with an oppositely charged layer and thus diminish its attraction on other systems. Thus, for example, in an aqueous solution of $CaCl_2$ the positively electrified part of the calcium atom would have next to it the negative ends of polar water molecules, and the attraction between it and an oppositely charged chlorine atom would be diminished. The researches of Mr. Washburn furnish direct experimental evidence of the hydration of ions.[17]

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[17] *Technology Quarterly,* 21, p. 288 (1908).

CHAPTER IV.

THE MECHANISM OF CHEMICAL COMBINATION.

LET us in the first place consider chemical combinations between gases. That something more than collisions between the molecules of the reacting gases is required is clear, from the fact that gases like hydrogen and oxygen, hydrogen and chlorine (in the dark), which can form very stable compounds, can be mixed without any appreciable amount of chemical combination taking place at moderate temperatures. The test is a very severe one since at atmospheric pressure each molecule of oxygen in a mixture of hydrogen and oxygen would in one second collide with many million hydrogen molecules, so that even if only one collision in a million were to result in combination the rate of combination would be very great. A mixture of hydrogen and oxygen in the proportion of two molecules of hydrogen to one of oxygen can be stable, (*a*) when the gases are uncombined, and (*b*) when they are combined and the mixture exists as water vapour. The large evolution of heat observed in the transit from (*a*) to (*b*) shows that (*b*) has much less potential energy than (*a*). The fact that the gases can exist side by side without combination shows that the phase of high potential energy does not spontaneously pass to one of lower. We have many examples of this in ordinary mechanics. Thus the water in a mountain lake has more potential energy than it would have if it ran down into the valley, it does not do so because before it could get away work would have to be supplied to raise it above the level of the height immediately surrounding it. If a syphon is put into the lake this work is forthcoming and the water will run out. To enable a system to pass to a state of smaller potential energy may require the expenditure of a certain amount of energy and if this is not forthcoming the change will not take place. Thus, if a preliminary to the combination of hydrogen and oxygen were the dissociation of the molecules of these gases into atoms, the gases would not combine unless the very considerable amount of energy required for this initial stage were available. Now in the mixture of two pure gases the energy available is that due to the thermal agitation of the molecule; this at 0° C. is only about 1/30 of a volt per molecule, and is small compared with the changes in energy occurring in chemical processes which on the same scale would be represented by several volts. Thus we might expect that unless some source of energy besides that due to thermal agitation were available, the combination would not take place. In the case we have just been considering, that of the dissociation of electrolytes in solution, the main part of the energy required to separate the ions in the electrolyte came not from thermal agitation, but from that derived from the falling in of polar molecules, *i.e.,* from the energy of chemical separation of the polar molecule and the molecule of the electrolyte.

The effect of water vapour, whose molecule is strongly polar, on the combination of gases is well known. Thus, H. B. Baker showed that very carefully dried HCl and NH_3 would not combine, that the combination of H_2 and Cl_2 went on exceedingly slowly, even in strong sunlight, when the gases were carefully dried, while H. B. Dixon showed that electric sparks might be passed through a mixture of dry CO and O_2 without combination taking place. He also showed that other substances besides water vapour render possible the combination between CO and O, and it is probable that all polar molecules possess this property to a greater or less extent. Baker found that the effect of water vapour was not confined to combination. It extended also to dissociation, for while ordinary ammonium chloride is dissociated to a very considerable extent when the temperature is raised to three or four hundred degrees centigrade, no dissociation occurs at these temperatures if the salt is very carefully dried.

When polar molecules, such as those of water or ammonia, are present, they may combine with the other molecules, forming aggregates in which, as in the case discussed in a previous lecture, there is a kind of incipient ionization, the atoms being more widely separated than in the normal molecule. The aggregate has a finite electrical moment and thus exerts much greater forces on neighbouring molecules than the normal molecule. Let us represent these aggregates by $A(H_2O)_n$, $B(H_2O)_m$ when A and B represent molecules of the reacting gases. When two of these come together the work required to separate them may be so much greater than that required to separate AB that though A and B cannot by collision form a potent aggregate $A(H_2O)_n$ and $B(H_2O)_m$ are able to do so. After the aggregate has been formed the atoms, loosened by the action of the polar molecules, rearrange themselves so as to produce the system with the minimum potential energy. If, as the result of this rearrangement, the water is set free, it will be available for producing a further supply of the complex molecules. Even if only a small percentage of the molecules are in the complex state the rate of combination might be considerable, as the number of collisions made by a molecule under ordinary circumstances is so large. Thus to take the combination of gaseous HCl and NH_3 to form NH_4Cl as an example. If even only one molecule in a hundred thousand were in the complex state and if the combination only occurs when a complex molecule of HCl collides with a complex one of NH_3, these collisions will still be so numerous that something like one per cent. of the HCl and NH_3 will combine per second. We see from this that to avoid appreciable combination the gases must be exceedingly dry, and that traces of water too small to be detected by other means might produce very marked effects on chemical combination.

On this view of chemical combination the rearrangement of the atoms takes place inside a complex formed with the polar molecules, thus no ions need get free. There is very strong evidence against the necessity for the existence of free ions in gaseous combinations; free ions make a gas a conductor of electricity and the conductivity due to free ions can be detected when the number of free ions is much less than one-million-millionth of the number of molecules. Many cases of chemical combination have been tested for electrical conductivity without any trace of it being detected. Thus L. Bloch[18] showed that many chemical actions which go on at moderate temperatures, such as the oxidation of nitric oxide, the action of chlorine on arsenic, the oxidation of ether vapour and so on, have no effect on the electric conductivity of the gases. I found, too, that even when the combination was as vigorous as that between hydrogen and chlorine in the light, no effect whatever was produced on the electrical conductivity of the mixture. Again dissociation at moderate temperatures such as that of nickel carbonyl at about 100° C. into nickel and carbon monoxide, or in the dissociation of arseniuretted hydrogen, is quite without effect on the conductivity. This is in accordance with the consequences of the theory.

There are, however, some cases in which free gaseous ions are produced by dissociation or chemical action. Thus Kalendyk[19] found that the vapour of potassium iodide was a conductor of electricity at temperatures above 300° C. if damp, but not when dry; this is a good example of the effect of water vapour. Another case investigated by Bloch (*loc. cit.*) is the oxidation of P_2O_3 to P_2O_5, which is also accompanied by an increase in electrical conductivity.

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[18] *Annales de Chimie et de Physique,* **22**, pp. 370, 441; **23**, p. 28.

The efficacy of polar molecules is on this view due to their large electrostatic moment, which causes them to be strongly attracted by other molecules. Any systems, such as free electrons or gaseous ions, which give rise to strong electric fields, might be expected to promote chemical combination by processes similar to those which occur with water molecules.

Again, if the reacting gases were condensed on the surface of a piece of metal, or on the surface even of a non-metal or liquid, particularly if these substances were of special types, the molecules would find themselves in the presence of agents of the kind we are considering. At the surface of a metal there are mobile electrons, while the molecules at any surface can only be coördinately saturated in very exceptional cases. For when a new surface is produced by fracture some of the atoms which helped to " satisfy " the molecules left behind have been torn away, so that the molecules on the surface must be unsaturated and able to bind other atoms or molecules. The energy derived by the approach of a molecule to the unsatisfied molecules at the surface of the solid or liquid may be used to separate the atoms in the approaching molecule, in just the same way as the energy due to the approach of a polar molecule helped to separate them. Thus the molecules of a gas condensed in a layer on a surface will be exposed to influences very similar in character to those to which they would be exposed when combined with water molecules, and we may expect to find that the connection between these atoms gets so loose that these are able to rearrange themselves and form new compounds.

The layers condensed on a surface will in many respects be in a more favourable condition for entering into chemical combination than the free molecules of the gas, even if these are supplied plentifully with water molecules. For the molecules in the surface layer will be crowded together and kept in close contact; they will thus be in a situation particularly favourable for the rearrangement of their atoms.

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[19] *Proc. Roy. Soc.*, A90, p. 638, 1914.

The effect of metal surfaces in promoting chemical combination is shown by the combination of hydrogen and oxygen produced by platinum black, by the synthesis of ammonia in the Haber process, by the effect produced by metals when in the colloidal state, by the Sabatier-Senderens method, where many changes in organic compounds are produced by passing them along with hydrogen over finely divided nickel or certain other metals at a high temperature. Another instance is the effect produced by the walls of the vessel in which the reacting gases are contained; many examples of this are given by Van t'Hoff in his studies on chemical dynamics.

It is possible that water in addition to the effect it produces by its individual molecules may produce an additional effect by forming small drops, which in the aggregate might have a very large surface, on which the gases might condense.

We can get some very direct evidence as to the conditions at the surface of separation of gases, liquids and solids by the study of the very interesting cases of electrifications produced by the bubbling of gases through liquids, by the splashing of liquids against solid surfaces, and the motion under an electric field of bubbles of air, and colloidal particles through liquids. When gases bubble through certain liquids of which water is a conspicuous example, the gases after they emerge from the liquid are found to be electrified. The liquids which give rise to this electrification are those which possess considerable electrical moments, *i.e.,* they are those which, as we have seen, have the property of forming complex compounds with compounds which are already electrically saturated. The amount, and even the sign of the electrification produced by bubbling, is very sensitive to small changes in the composition of the liquid. Thus air bubbling through pure water emerges with a negative charge, but if a small quantity of HCl or H_2SO_4 be added to the water, the electrification of the air becomes positive. The electrification is dependent upon the breaking of the liquid film when the air bubble escapes from the fluid. No electrification is produced by blowing a current of air along a water surface or by stretching, without breaking, a liquid film. A similar dependence upon the composition of the liquid is shown by the motion through a fluid of small particles or air bubbles under an electric field, a phenomenon which is sometimes called cataphoresis. The addition of acids and salts, especially if these contain elements of high valency, produces a great effect on the velocity with which the bubble moves through a liquid under a constant electric field. Cataphoresis is more amenable to mathematical treatment than electrification by bubbling and the mathematical theory has been worked out by v. Helmholtz and Lamb on the supposition that there is a double layer of electricity, one layer being positive and the other negative, at the surface between the bubble and the liquid, and that one layer is attached to the liquid, the other to the bubble or colloidal particle. If v is the velocity of a particle under an electric force X, η the coefficient of viscosity of the liquid, σ the surface density of the electric charge on either layer, d the distance between the layers, then according to v. Helmholtz

$$v = \sigma d X / \eta \tag{29}$$

so that the measurement of the velocity would at once give us the potential difference at the surface. Lamb has given very strong reasons for thinking that this relation is not sufficiently general and is based upon suppositions which are not likely to be valid when, as in this case, we are dealing with distances which are of the order of atomic distances; he finds instead of (29) the equation

$$v = \sigma l X / \eta \tag{30}$$

where l is a length dependent on the liquid and on the nature of the particle. As l is not known, we cannot claim that the use of the v. Helmholtz formula gives more than the order of the surface density, in some cases, however, where it has been possible to measure the potential difference between the particle and water, this has been in fair agreement with the value deduced by Helmholtz's equation. It will be noticed that according to either formula the velocity of the particle is independent of its size, provided σd and σl are unaltered. This has been verified by several observers, among others by Burton[20] and McTaggart.[21] In water, air bubbles and some solid particles move as if the negative charge were on the particle, and it is remarkable that, in spite of great variations in the character of the particle, the changes in the potential difference are comparatively small. This is shown in the following table taken from Burton.[22] The potential difference φ has been calculated from the v. Helmholtz equation assuming

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[20] "Physical Properties of Colloids," 2nd Edition, p. 136.

[21] *Phil. Mag.*, 27, p. 297 (1914).

$$\varphi = 4\pi\sigma d/K \tag{31}$$

where K is the specific inductive capacity of water.

We see from this list that for many substances the difference of potential between the two layers is about 1/30 of a volt; this is very nearly the potential difference through which an electron must fall at room temperatures to acquire an amount of energy equal to that possessed by a molecule of gas from its thermal agitation. Thus a charged atom at the double layer would possess by thermal agitation an amount of energy comparable with that required to detach it from the double layer. We should expect that a limit to the potential difference between the two layers must be imposed by the necessity of one layer being able to move freely relatively to the other. If, for example, the double layer were formed by positively and negatively charged atoms in the same molecule it could not produce cataphoresis unless some source of energy sufficient to dissociate the positive from the negative parts were forthcoming. If this energy has to come from thermal agitation, the positive and negative parts must have been driven so far apart that the energy required to separate them is of the order of the mean kinetic energy of a molecule due to thermal agitation, which at 0° C. is about 1/30 of a volt. The energy required to detach a charge from the double layer is proportional to the potential difference between the layers. Thus the energy available from thermal agitation may be a most import-

Substance.	Potential Difference in Volts Deduced by Helmholtz's Equation.
Lycopodium	–.035
Quartz	–.042
Air bubbles	–.056
Arsenious sulphide	–.031
Prussian blue	–.056
Gold (Bredig)	–.030
Platinum (Bredig)	–.028 – .034
Silver (Bredig)	–.033
Mercury (Bredig)	–.035
Bismuth (Bredig)	+.015

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[22] "Physical Properties of Colloids," p. 135.

ant factor in determining the value of the potential difference in the effective double layer.

THE FORMATION OF THE DOUBLE LAYER.

Polar molecules, such as those of water, have, as we have seen, the power of forming molecular compounds in which oppositely charged atoms are separated and put into a condition in which they can be easily detached from each other. These compounds are of two types. In the first, symbolized by such a case as $[\mathrm{Me}\text{-}4H_2O.(OH)_2]H_2$, the effect of the formation of the complex compound is to give a charge of negative electricity to the substance with which the water is in contact and to put two positively charged atoms into a condition in which they can easily be detached from the substance. The formation of a compound of this type would produce a double layer with the positive part in the water and the negative on the substance. This is the type of double layer formed at the surface of colloidal particles of platinum, gold, silver, quartz or air bubbles. The other type of complex compound is that symbolized by $[Ca.4H_2O]Cl_2$, here the water molecules drive out the negative constituent from the original compound and give to the system surrounding the central atom a positive charge. If a substance of this kind were formed there would again be a double layer, but in this case the negative part of it would be in the water, the positive on the substance in contact with the water. This is the type of double layer formed at the surface of colloidal particles of ferric hydroxide.

The case of a gas bubble in water is an interesting one in which the evidence on some points is somewhat conflicting. McTaggart found that the velocity of bubbles of hydrogen was the same as that of oxygen bubbles indicating that the potential difference was independent of the nature of the gas, and that the gas did not take part in any chemical reaction. Alty, who has recently been making experiments on this point in the Cavendish Laboratory, finds that considerable variation in the velocity of the bubbles is produced in some cases by changing the gas. The view that oxygen may take part in chemical reactions with water is supported by the observation frequently recorded but first made, I think, by Bèllucci,[23] that the air in the neighbourhood of water-falls, where there is a great deal of splashing, contains abnormally large quantities of ozone. Under the action of the water molecules ozone may be formed and negatively electrified ozone form the coating in the gas of the double layer.

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[23] *Ber. Deutschen Chem. Gesell.*, 8, p. 905 (1875).

We should expect that there would be a double layer at a surface separating water from its own vapour. Hardy and Langmuir have pointed out that the molecules at a liquid water surface are polarized, *i.e.*, the number of molecules which have their positive ends at the top is not the same as the number with the negative end. Thus, suppose the majority of molecules had the negative ends, *i.e.*, the oxygen atom, at the top, the oxygen atoms are not coördinately saturated and may combine with the molecules of water vapour to form compounds of the type $[O.H_x](OH)_x$: This would give rise to a double layer with the positive half in the water, the negative one in the bubble. Experiments are in progress at the Cavendish Laboratory to see whether any evidence can be obtained of a double layer when water is in contact with nothing but water vapour.

The formation of the double layer gives a supply of positive and negative ions at the surface of an air bubble in water. Just before the bubble emerges from the water this surface has a considerable area. It is reduced to very small dimensions after the bubble emerges. Thus the emergence of the bubble involves a considerable and very abrupt contraction of the surface and of the double layer associated with it. The double layer will be violently distorted and it does not seem surprising that some of the ions in the layer on one side should not have time to combine with those on the other before they are carried away by the air. Only a very small fraction of the ions in the double layer get liberated when air bubbles through water. Assuming v. Helmholtz's formula, we can calculate from the velocity of the bubble the quantity of electricity per unit area of each layer. Assuming that the distance between the layers is 10^{-8} cm., McTaggart (*loc. cit.*) found that this density was 4×10^{-5} coulombs per square centimetre. If all the water molecules had been polarized, *i.e.*, if all the OH ions of the water molecules were next the surface and if the distance between two molecules of water on the surface were the same as that in the interior, *i.e.*, 3.09×10^{-8} cm., the density would be about 1.7×10^{-4} coulombs per square centimetre, about four times greater. On one layer of a bubble 7.8 mm. in diameter the charge on either layer would be 7.6×10^{-5} coulombs. Simpson[24] found that when a drop of this size struck against a plate the amount of electricity set free was 2.8×10^{-12} coulombs, *i.e.,* only about one thirty-millionth of the charge on the layer. We conclude from this that only an exceedingly small fraction of the water molecule at the surface of an air bubble or drop of water is ionised by the bursting of the bubble or the splashing of the drop.

When air bubbles through water some ions become free, there are other types of experiments when, though there is a separation of positive and negative electrification, few if any ions get free. The Armstrong hydro-electric machine is a case in point. Here small drops of water are carried by a jet of steam through a tube with great velocity. In their passage through the tube the drops strike against the sides and the tube becomes negatively, the drops positively, electrified. Here the separation of the positive and negative electrification is the principal effect and not the liberation of free ions. We have supposed that at the surface of a drop of water there is a double layer, the negative part, OH ions, in the air and the positive part, H ions, in the water. When the drop strikes against the tube the OH ions combine with the material of the wall of the tube forming those molecular compounds we have been considering in this chapter. When the drop rebounds from the wall of the tube it will tend to take the H_+ ions away with it, while the walls of the tube will hold the OH_- ions. The ions will be separated by the kinetic energy of the drops. The ions will not, however, get free; the positive ones will be on the water drops and the negative ones on the walls of the tube. This is a particular case of electrification by friction, and it is evident that the formation of double layers must be of vital importance in that phenomenon

ACTIVE MOLECULES.

We have considered the way in which chemical combination may be promoted by polar molecules and by active surfaces, the energy necessary for the preliminary separation of the atoms in the reacting molecules before their final readjustment to form the molecules of the new compound coming from the potential energy of separation of the polar molecules and of the reacting molécules before combination. We have seen that the kinetic energy of thermal agitation is inadequate for this purpose. Though the influence of polar molecules on chemical combination is undoubtedly very great, the evidence does not, I think, warrant the conclusion that all chemical combinations are dependent upon their agency. The combustion of carbon bisulphide, of cyanogen and of certain hydrocarbons in oxygen appear to be unaffected by the presence of traces of moisture.[25] The question arises, what is the mechanism by which the combination can be brought about, when the energy arising from polar molecules is not available, and when that due to thermal agitation is too small to split up the molecules of the reacting gases into atoms? The electron theory indicates a way in which certain molecules could be put into a chemically active state without separation into atoms by an expenditure of energy much less than would be required for that purpose. Consider, for example, a molecule of oxygen, its neutrality is attained by the arrangement of its electrons into two octets, to obtain these two the utmost economy in construction must be observed and the octets have to have four electrons in common. Let the electrons in the molecule be displaced so that the cells surrounding the atoms have no longer four electrons in common, suppose, for example, that they have only two in common, then since there are only twelve electrons available there can only be seven electrons in each cell, and each atom will be surrounded by only seven electrons instead of by eight. Now the cell of seven electrons is not saturated and will be chemically active, though it will not be so unsaturated as the free oxygen atom which is only surrounded by six electrons. To move the electrons so as to change the arrangement of electrons from that corresponding to the inactive state represented by Fig. 35 to that of the active state represented by Fig. 36 would require far less energy than to separate the atoms, so that the necessary amount

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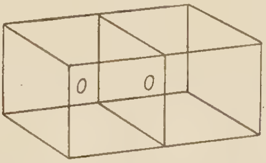
[24] *Phil. Trans.,* 209A, p. 379 (1909).

FIG. 35.



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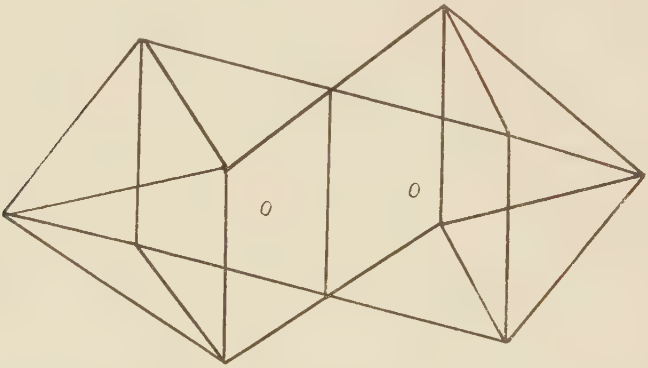
[25] H. B. Baker, *Proc. Manchester Phil. Soc.*, 53, No. 16.

may be derivable from thermal agitation at temperatures far below that required to separate the atoms.

I think this conception of the active molecule has an important bearing on the combination of explosive mixtures such as those of oxygen and hydrogen; these gases explode at temperatures as low as 600° C. where the energy of thermal agitation is quite insufficient to split the oxygen molecules up into atoms. Indeed, direct experiments on the relation between temperature and pressure have shown that there is no appreciable dissociation of the molecules of oxygen at 1700° C. If, however, the work required to make the molecule active in the manner described was that corresponding to thermal agitation at a lower temperature, say 600° C., then if in any region of a mixture of the explosive gases the temperature reaches this value, the oxygen molecules will become active and combine with the hydrogen, the heat developed by the combination will raise the temperature still further and the hot molecules will travel out with energy sufficient to make the molecules of oxygen against which they strike active. This will lead to further combination and a further development of heat and combination will spread throughout the mixture.

FIG. 36.



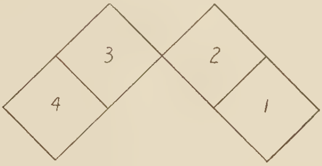
As there is no dissociation of the molecules into atoms, the process of making the oxygen molecules active will not change the pressure in pure oxygen.

There is direct experimental proof that the molecule of oxygen can be put into the active state. For when we use the method of positive rays we find that oxygen is one of the few molecules, as distinct from atoms, that can occur with a negative charge. If the oxygen molecule could only occur with its electrons arranged as Fig. 35, it could not receive a negative charge, because there is no room for an electron in the octets. It could, however, receive such a charge if the electrons were arranged as in Fig. 36 because there is room for an electron on each of the septets.

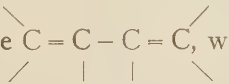
The fact that a particular atom or molecule can be negatively charged, shows that it can be in stable equilibrium after receiving an additional electron, so that in the neutral state it must be unsaturated and chemically active.

The arguments we have used about the oxygen molecule will apply to any arrangement of electrons where there are two octets with four electrons in common. This arrangement occurs when we have two atoms connected by a double bond—it occurs, for example, in carbon compounds whenever there is a double bond between two carbon atoms, $C = C$, it also occurs in the combination $C = O$, though not in $C — O - H$.

FIG. 37.

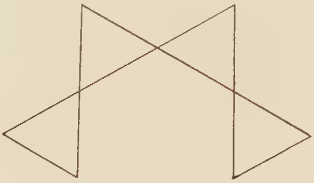


THIELES' THEORY OF PARTIAL VALENCIES.

This conception of the active molecule leads in many cases to the same results as Thieles' theory of partial valencies. Thus to take the case which led to the theory. It was found that a compound where the carbon atoms are arranged according to the scheme  $\overset{\diagdown}{\underset{\diagup}{C}} = \underset{|}{C} - \underset{|}{C} = \overset{\diagup}{\underset{\diagdown}{C}}$, where two double bonds are separated by a single one, when it forms additions compound does so by adding the new atoms to the carbons at the *ends* of the chain. On our view the distribution of the electrons in the compound is represented in Fig. 37.

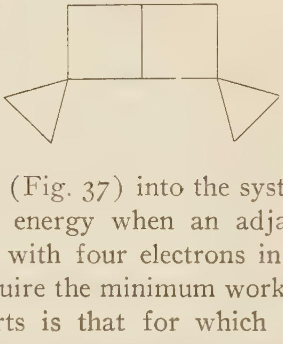
There are four octets, 1, 2, 3, 4; 1 and 2 and also 3 and 4 have four electrons in common, 2 and 3 only two. Suppose all the carbon atoms get put into the active condition. The octets with four electrons in common will become septets with two electrons in common and the system will be a chain of four septets (Fig. 38), where the septets are represented by triangles, each having two electrons in common with its nearest neighbour. To make this change in which all the carbon atoms have been made active requires the expenditure of a certain amount of energy; an expenditure of a smaller amount will be sufficient to make a part of them active. To find the change which will require the least energy, we notice that if any adjacent pair of septets were to revert to a system with four electrons in common, the new system would have less potential energy than that shown in Fig. 38, and would require less energy to be expended to derive it from the original system.

FIG. 38.



The work required for this change would be the work required to convert the system (Fig. 37) into the system (Fig. 38), minus the loss of potential energy when an adjacent pair of septets reverts to two octets with four electrons in common. Thus the system which will require the minimum work will be the one when the pair which reverts is that for which the loss of potential energy on reversion to octets is greatest. This pair will be the one which is most symmetrically placed, *i.e.,* the central pair. Thus the active configuration which requires the least expenditure of work is that represented in Fig. 39, where the end cells are septets and active. As these cells are active, additions will take place at them, and the central carbons will be connected by a double bond.

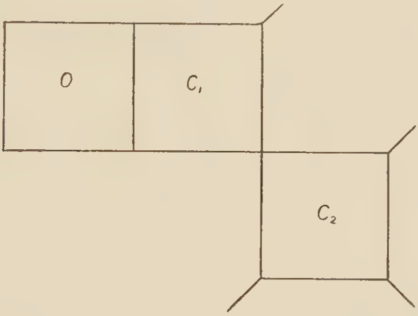
FIG. 39.



KETO-ENOL CHANGE.

The same reasoning will apply where the double bond is between a carbon and an oxygen atom. Thus in the compound $O = \underset{|}{C} - \underset{\wedge}{C} - H$, the distribution of electrons is that represented in Fig. 40, if the two octets with four electrons in common are made active, the active oxygen units with the neighbouring atom of H, the hydrogen coming away from C_2 with its electron; this completes the octet round O, leaving septets round C_1 and C_2 with two electrons in common; these revert to the more stable arrangement of the same number of electrons, *viz.*, two octets with four electrons in common, and we have thus the compound

FIG. 40.



$$OH - \underset{|}{C} = \underset{\wedge}{C}$$

this is known as the keto-enol change. It only takes place when one of the atoms attached to C_2 is that of an electronegative element; the reason for this follows from the same considerations as those previously given (p. 61) to explain the effect of introducing electronegative groups into hydrocarbons.

The same principles will apply to a smaller extent when two octets have only two electrons in common, for if the electrons were displaced so that the cells had only one electron in common, one of the atoms would become active and could enter into chemical combination. Thus, if the electrons in a chlorine molecule get displaced so that the cells have only one electron in common instead of two, one of the cells will become active and can combine with hydrogen. The energy required to displace the electrons need not come from the energy of thermal agitation, it might come from light if that were absorbed by the molecules.

PRODUCTION OF LIGHT BY CHEMICAL CHANGE.

Many chemical reactions involve an increase or a decrease in the number of electrons grouped round some of the atoms; thus, for example, if an atom of hydrogen combines with one of chlorine to form HCl, after combination the chlorine atom is surrounded by eight electrons, whereas before it was surrounded by only seven, thus the reaction has resulted in an electron falling into the layer round the chlorine atom; this atom may be regarded as coming from the hydrogen atom. On the other hand, when HCl dissociates into H and Cl the chlorine ion loses an electron, while the hydrogen ion gains one. We shall use the term oxidation for the process by which the atom of an electronegative element gains an electron and becomes negatively charged since ordinary oxidation is a process of this kind, and reduction for the process by which a positively electrified ion of an electropositive element receives an electron and becomes neutral.

Thus, in oxidations an electron falls into the zone round the atom of an electronegative element; in reductions an electron falls into the zone round the atom of an electropositive one. From the study of the luminous effects in the discharge of electricity through gases we are led to the conclusion that the capture of an electron by an atom results in the emission of light, and from the quantum theory it would follow that the frequency of the light would be proportional to the potential energy lost when the electron falls into the atom, or what is equivalent, to the work required to remove an electron from the negatively electrified constituent of the compound in the case of oxidation or from the neutral atom in that of reduction. Thus we should expect that both oxidation and reduction would be accompanied by the emission of light; it may be that the rate at which the chemical processes go on is so slow that the energy in the light is not sufficient to make it apparent, or again, that the wave-length of the light is not within the range of the visible spectrum. The production of light by chemical action is a well-known phenomenon. In addition to the conspicuous cases of flames where the temperature is high, there are many examples of luminosity occurring at moderate temperatures; the luminosity of phosphorus when oxygen passes over it is one example; then there is the luminosity of sulphur when heated to about 300° C. in the presence of oxygen, the light given out by the glowworm and by the animalculæ which cause the phosphorescence of the sea. Linneman found that fresh surfaces of sodium or potassium are luminous in the dark until they get covered by a coat of oxide. This production of light is, I think, the cause of the emission of electrons in the dark from the alloy of sodium and potassium when exposed to various gases which I observed many years ago and which has been investigated very fully by Haber. If chemical action went on between the gases and the NaK alloy, light would be given out, and as the alloy is very photoelectric, electrons would be given out by the surface of the alloy. The seat of the light is at the surface of the alloy so that, although the light might not be intense enough to be visible at molar distances, yet at the atomic distances which separate its source from the alloy its intensity might be sufficient to produce very considerable effects. Again, since in oxidations the origin of the light is in the electronegative elements, we should not expect to find in light due to oxidation the spectrum of the electropositive element. It has long been considered remarkable that the spectrum of hydrogen is not visible in flames or in light produced by chemical means, though it is so easily produced by the electric discharge. This is just what we should expect if the chemical reactions were of the type of oxidations; to have a chance of getting the hydrogen spectrum the process should be a reduction. Thus, for example, in the partial dissociation of hydriodic acid, when there is equilibrium between the formation of HI and its dissociation into H and I, the combination would give rise to the spectrum of HI with the iodine as the source of light, the dissociation might give the hydrogen spectrum. It is to be noted that the spectrum of a molecule may vary with the atom in that molecule which is excited. Thus to take as an example $COCl_2$, the spectrum emitted due to the fall of an electron into the oxygen atom would not be the same as that due to the fall of one into the chlorine atom. We have in considering the type of light emitted to consider not merely the atom into which the electron falls, but also the method in which it falls. Thus take a case in which we have very vigorous reduction going on, that of the liberation of hydrogen from the cathode when strong currents pass through acidulated water, since the hydrogen atoms which come off are neutral, the hydrogen ions which were positively electrified must each have received an electron and so might be expected to have given out light. I am not aware, however, that anyone has observed any luminosity in the neighbourhood of the cathode during the electrolysis of acidulated water. Nor need we, I think, expect it; we have already seen reasons for thinking that hydrogen ions in water have attached to them a number of water molecules, the negative ends of these molecules being turned towards the hydrogen ion. The effect of these negative charges is to diminish very materially the attraction of the hydrogen ion on the negative electron, so that when the electron falls into the ion it will do so with very much less energy than it would in the absence of the water molecules; as the energy is so much less, the intensity of the light and also its frequency will be greatly diminished, so that not only will the light be feeble, but also probably far away, on the red side of the visible spectrum.

ON HOMOLOGOUS ELEMENTS AND VARIABLE VALENCY.

Homologous Elements.—The valency of an element depends according to these views on the number of electrons in the outer layer rather than upon the total number of electrons in the atom. We have supposed that the electrons in the atom are arranged in a finite number of layers, the members of each layer being approximately at the same distance from the centre of the atom. As we pass from the atom of one element to that of the element next in order of atomic weight, we have to provide for the accommodation of one more electron in the atom. If the additional electron joins those in the outer layer it will give rise to an atom of an element of different valency and with very pronounced difference in chemical properties. If, however, the electron finds accommodation in one of the layers below the surface, the element corresponding to this atom will have the same valency as the first and will resemble it in chemical properties more or less closely according as the layer on which the new electron settles is near to or far from the centre of the atom. Thus we might have a graduated series of elements differing in atomic weight; the properties of some—those with the additional electrons in the layers close to the centre differing so little from those of some element of smaller atomic weight in the series that the two might with propriety be regarded as isotopes. The difference in properties will increase though the valency remains unaltered, as the electrons find a place in layers nearer the surface until finally we come to the element where the additional electron has got to the outer layer; here there is a change in the valency and a marked alteration in the chemical properties. We are thus led to expect the existence of groups of elements possessing very similar properties; in some cases the chemical properties might be so similar that the elements would not be separable by chemical means and would be classed as isotopes; in others the differences would be large enough to enable the elements to be isolated by chemical processes. Examples of such groups are the iron, nickel and cobalt group, the ruthenium, rhodium and palladium group, the large group of the rare earths and the iridium platinum group. Inside these groups, increase in atomic weight is not accompanied by change of valency; outside them, it is.

In considering the way in which a definite number of electrons will arrange themselves round a central charge, there are two influences of predominating importance: The first of these is the tendency of the electrons to get as close to the central charge as is consistent with the stability of the layer, *i.e.,* to have as many electrons in the innermost layer as the central charge can hold in stable equilibrium, and then as many in the second layer as the central charge when surrounded by the first layer can hold in stable equilibrium, and so on. This disposition will make the potential energy due to the forces between the positive nucleus and the electrons as small as possible. The potential energy due to the forces between the electrons has next to be considered. This will diminish as the distances between the electrons increase and will tend to make the electrons in the various layers arrange themselves so that their figures are similar, or at any rate have the same kind of symmetry about the centre. This latter tendency would, if it prevailed, cause a new electron if added to an atom already containing a number of electrons either to go to the outer layer, or if that were full, to make the beginning of a new outer layer. The tendency to get as close as possible to the centre would, on the whole, make for the retention of the electron by one of the inner layers.

We should expect that we could not go on increasing the number of electrons without reaching a stage where a new electron would stay in the inner layers. If so, its influence on the chemical properties would be very slight and the new element would be very similar to the old. The addition of an electron to one of the inner layers would alter the nature of its symmetry round the centre and make it different from that of the other layers; as the different layers like to have the same kind of symmetry, when one layer has got a new electron the others will try to get one, too, so that when once the absorption of electrons by the inner layers has begun it will continue as the next few electrons are added to the atom. When each layer has received an electron, we may expect the next electron to come to the surface, giving rise to an element whose properties are markedly different from those of the elements which just preceded it. Thus the homologous elements might be expected to occur in groups and inasmuch as in the elements inside the group, some of the layers have one kind of symmetry and others a different one, the distribution of electrons inside the atom of elements in a homologous group is irregular and does not possess the uniformity or regularity possessed by elements outside the group where the electrons in the inner layers have adjusted themselves so as to produce a high degree of symmetry.

Varying Valency.—We have been considering cases where different elements have very similar chemical properties, although they contain different numbers of electrons, where, in fact, we have variations in the number of electrons in the atom without much alteration in the chemical properties. The question naturally arises whether we might not have also variation in the chemical properties without alteration in the number of electrons, and whether the existence of some elements which have more than one kind of valency is not a case in point. Ferrous and ferric iron have different properties, so have cuprous and cupric copper. As the elements can pass backwards and forwards between the -ous and the -ic states, if these states correspond to two different configurations of the same number of electrons, these configurations must be such that by suitable chemical or physical processes they can pass from one form to the other. We have already seen that there are frequently more ways than one of arranging in stable equilibrium a given number of electrons round a central positive core. If these arrangements are to explain the difference between the -ous and -ic states of the elements, they must differ in the arrangement of the outer layer (*a*) because unless they did so there would not be sufficient difference in the chemical properties in the two states, and (*b*) because if the difference was only in the inner layers we could not affect these sufficiently by ordinary chemical operations to cause one configuration to pass into the other.

We should expect, I think, to find forms of the same kind of atom differing in their outer layers in those elements which are either in a group of homologous elements or in their immediate neighbourhood. For in the atoms of such elements an electron hesitates, as it were, whether to go to the surface or to stay in one of the inner layers, *i.e.*, it hesitates between two different configurations. It is reasonable to suppose that by suitable influences at the surface the electron might be induced to take one course or the other and thus confer one valency or another on the atom of which it is an occupant. Now it is remarkable that many of the elements which are most conspicuous for the variability of their valency are either in the homologous groups or in their immediate neighbourhood. Take, for example, chromium and manganese, which are the next neighbours of the iron groups, each of these shows great variations in valency in its different compounds, then molybdenum, the next neighbour to the ruthenium, rhodium and palladium group forms the series of chlorides $MoCl_2$, $MoCl_3$, $MoCl_4$, and $MoCl_5$; again tungsten, the next neighbour to the platinum and iridium group, forms the four chlorides WCl_2, WCl_4, WCl_5 and WCl_6, and nearly, if not quite, all of the elements in the homologous groups themselves form more than one series of salts. The electrons in the outer layers of elements of this type seem to be in a peculiarly sensitive condition and can move from one layer to another without much expenditure of energy.

The number of electrons which can be held in stable equilibrium in a single layer by a positive charge increases with the charge. Thus, though an inner layer of eight might be as many as the positive charge possessed by the lighter elements could stabilize, yet the heavier elements with their large positive charges might be able to stabilize more than this number. We should thus expect that at some stage in the list of elements the number of electrons in the inner layers would increase, that while when we pass from one element to the next and the number of electrons in the atom increases the additional electron stays in the inner layer instead of going to the one on the outside of the atom. When this process begins the change from atom to atom will not be the addition of an electron to the outer layer, but a reorganization of the distribution of electrons in the interior of the atom. The properties of the elements indicate that this process begins soon after passing calcium. To illustrate the point, I will take the series of elements beginning with titanium and consider the arrangement of electrons in it and the neighbouring elements. I do not lay any stress on the actual numbers of electrons assigned to the inner layers; the determination of these would require much further investigation, both theoretical and experimental.

Titanium.—The distribution of electrons, if it followed the same course as in the lighter elements, would be represented by 2, 8, 8, 4, the figures representing the number of electrons in the different layers starting from the inside; the four electrons in the outer layer would make the element quadrivalent. The existence of the tetrachloride $TiCl_4$ shows that this distribution is one which occurs in nature. In addition to the tetrachloride there are the chlorides $TiCl_3$, $TiCl_2$, showing that forms of the titanium atom exist in which there are respectively one and two more electrons in the inside than in quadrivalent titanium, the distribution of electrons in the tautomeric forms may be represented by 2, 9, 8, 3, and 2, 10, 8, 2, respectively.

Vanadium.—If the electrons had followed the normal course, the arrangement of the electrons would be represented by 2, 8, 8, 5, and the element would be pentavalent. Vanadium is said to form a pentafluoride VF_5, so that this configuration would seem to exist. Vanadium forms chlorides VCl_4, VCl_3, VCl_2, in which the inner layers of the atom must contain respectively one, two and three electrons more than the preceding case; thus we have atoms in which the arrangements are 2, 9, 8, 4; 2, 10, 8, 3; 2, 10, 9, 2, respectively.

Chromium.—If the electrons followed the normal course the arrangement would be 2, 8, 8, 6, and the element would be sexavalent; the compound CrF_6 shows that this type exists. Chromium forms the chlorides $CrCl_3$, $CrCl_2$, so that in addition there are atoms of the type 2, 11, 8, 3; 2, 12, 8, 2, respectively.

Manganese.—The normal arrangement would be 2, 8, 8, 7. The fluoride MnF_7 shows that this type exists. There are in addition the fluorides MnF_4, MnF_3, MnF_2, corresponding to atoms of the type 2, 11, 8, 4; 2, 12, 8, 3; 2, 12, 9, 2.

Iron, Nickel and Cobalt.—From the similarity of these elements we infer that the distribution of electrons only differs in the inner layer, Their halogen compounds are all of the type $FeCl_2$ or $FeCl_3$; suggesting the following distribution of electrons:

Fe	2, 12, 10, 2.	2, 12, 9, 3
Ni	2, 13, 10, 2.	2, 13, 9, 3
Co	2, 14, 10, 2.	2, 14, 9, 3

Copper.—The halogen compounds are of the type CuCl, $CuCl_2$, indicating atoms with one or two electrons, respectively, in the outer layer, corresponding to distribution of electrons represented by 2, 14, 12, 1; 2, 14, 11, 2.

The normal process by which, when we pass from one element to the next in order of atomic weight, the new electron goes to the outer layer seems to be resumed after passing copper, thus we have zinc with two electrons in the outer layers; gallium with three; germanium with four; arsenic with five; selenium with six; bromine with seven, and krypton with eight.

Thus we see that as we proceed up the list of elements we may expect to meet with a batch of elements in whose atoms the electrons change from one tautomeric distribution to another with but little expenditure of energy. In this batch the ordinary progress of valency with atomic weight is interrupted, and the valencies are variable. On passing through the batch the regular sequence is resumed, the series goes on and ends with eight electrons on the outer layer, while the next series begins with one in that layer.

Paramagnetism.—One very conspicuous feature of the elements from titanium to copper is that they are strongly paramagnetic. The quality of paramagnetism would on several theories depend on a want of symmetry in the arrangement of the electrons in the atom. This would be the case, for example, in Parson's theory of the ring electron; it would also follow from the law connecting electrostatic and magnetic force which I suggested some time ago.[26]

If want of symmetry in the distribution of electrons is essential for paramagnetism, we can understand why it is confined to elements such as those we are considering, where the arrangement of the electrons in the inside of the atom may change, not merely from element to element, but even in a particular element under different external conditions. Outside such a group of elements the arrangement of the inner electrons does not change from element to element, it is very stable, and thus has probably a high degree of symmetry. It would, from this point of view, be interesting to test whether compounds of magnetic metals like CrF_6 and MnF_7, in which the readjustment of the inner electrons has not taken place are magnetic.

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[26] *Phil. Mag.*, 37, p. 419.

The researches of G. Wiedemann, Quincke, Townsend, Pascal, Weiss, Kamerlingh Onnes and others on the relation between magnetic properties and chemical composition have brought to light a great number of very striking phenomena, which are very diverse and in some cases anomalous, their very diversity, however, renders them all the more suggestive.

For salts in solution, and the same seems to be true for salts in the dry state, especially if these contain water of crystallization, the value of k, the coefficient of magnetization, *i.e.*, the quotient of the induced magnetization by the magnetic force, depends upon whether the metal is in the *-ous* or *-ic* state, but does not depend upon the acid radicle with which it is combined. Thus if a solution contains a definite amount of ferric iron the value of k will be determinate, it does not matter whether the dissolved salt is ferric chloride, ferric sulphate or ferric nitrate. The same is true for the ferrous salts; again the value of k depends only on the quantity of ferrous iron, but the value of k for the same weight of iron will depend upon whether the iron is in the ferrous or ferric state. Thus if W is the weight of iron in a cubic centimetre—

$$10^7 k = 2660W - 7.7 \text{ for ferric salts.}$$

$$10^7 k = 2060W - 7.7 \text{ for ferrous salts.}$$

In such salts as ferrocyanide of potassium where the iron appears on the negatively electrified part of the molecule, thus $\overset{+}{K_4}(\overset{-}{FeCN_6})$, the compound is not paramagnetic at all, but slightly diamagnetic. The ferricyanide $K_3(FeCN_6)$ is slightly paramagnetic, although the paramagnetism is very small in comparison with that of the ferrous or ferric salts. Similar results are shown by the magnetic metals Cr, Mn, Ni, Co. Copper itself is diamagnetic as are also the cuprous salts; the cupric salts, however, are magnetic. The oxides and sulphides of the magnetic elements show large variations in their magnetic properties, thus magnetite Fe_3O_4, which is regarded as a compound of FeO and Fe_2O_3, is much more magnetic than either of them, and a similar statement is true for the corresponding sulphur compounds. Again variation in the temperature may produce great changes in the magnetic properties of an element, thus four types of iron, α, β, γ, δ, have been detected by Osmond and other workers; these pass from one into the other when the temperature passes through definite stages, and each of these types of iron has characteristic magnetic properties. In discussing the meaning of these results we must remember that on the view that paramagnetic properties are due to the setting of magnets, or their equivalents, under the action of a magnetic force; the magnetization, unless the field is intense enough to produce saturation (a state of things which is not attained with solutions), will depend upon two quite distinct things: (*a*) The resultant of the moments of the magnets; (*b*) the restoring force which tends to keep the magnets in the position of equilibrium. A substance may have a small coefficient of magnetization either because it contains few magnets or because the restoring force is very great, so that a given external field produces but a small displacement of the magnets. Thus the difference between the coefficients of magnetization of ferrous and ferric iron may be due either to the difference of the magnetic moments of the magnets in the atom in the two states or to a difference in the restoring force. If it is due to a difference in the magnetic moments the intensity of magnetization when the ferrous iron is saturated will not be the same as when the ferric iron is saturated, whereas if it is due entirely to the difference in the restoring force the saturation magnetization will be the same in the two cases. We can distinguish between these effects by Weiss' Theory of Magnetons as the number of magnetons is proportional to the magnetic moment. The result of the application of this theory is that the number of magnetons per atom of iron in ferrous sulphate is 27, in ferric it is 29. As the coefficient of magnetization differs more widely than these numbers, it follows that the restoring forces must be different in the ferrous and ferric salts. In the iron in potassium ferricyanide Weiss finds that there are only ten magnetons. The difference between the number of magnetons in the trivalent and divalent condition is more pronounced in chromium and cobalt than it is for iron, thus for trivalent chromium the number of magnetons is 19, for divalent 25, in trivalent cobalt the number is 17, in divalent between 24 and 26; thus in both these metals the number of magnetons in the divalent condition is greater than in the trivalent, whereas in iron the trivalent form is slightly richer in magnetons than the divalent. A very striking case of the variation of the number of magnetons with chemical composition is that of the oxides and sulphides of vanadium. Wedekind and Horst [27] give the following values for *k* the coefficient of magnetization and *n* the number of magnetons in various compounds of vanadium.

	$k \times 10^6$	n
VO	50.06	13.9
V_2O_3	13.88	10.92
VO_2	3.73	4.19
V_2O_5	0.86	2.99
VS	7.22	5.86
V_2S_3	8.95	10.00
V_2S_5	12.55	11.90
VOCl	27.16	13.18
VN	4.13	3.92

Thus the effect of oxygen is of the opposite character to that of sulphur, an increase in the oxygen content decreases, while an increase in sulphur content increases the number of magnetons.

Let us now proceed to see how the magnetic properties of the salts of the magnetic metals are consistent with the following assumptions:

1. That the paramagnetism of these substances arises from the atoms of the paramagnetic element. Fe. Cr. Mn. . . .

2. That the magnetic properties of these atoms arise from a want of symmetry in the distribution of the electrons in the inner layers.

3. That the distribution of these electrons and therefore the symmetry of their arrangement can be affected by intense electric forces arising from atoms with their electrons in the neighbourhood of the atom of the magnetic element, and that such forces may also affect the restoring force of the electrons in the atom, *i.e.*, the force with which the system of electrons resists any displacement from their position of equilibrium.

We shall take in the first place the very large diminution in magnetic properties which takes place when the atom of the magnetic element is a constituent of a complex salt such as $K_4(FeCN_6)$ ferrocyanide of potassium. We may point out that this diminution may take place when the magnetic element occurs in a complex with the positive charge and not merely when as in $K_4(FeCN_6)$; the iron is a member of the negatively electrified group. Thus Feytis[28] has shown that the following cobalt salts are diamagnetic—$(Co(NH_3)_6)Cl_3$, $(Co(NH_3)_5Cl)Cl_2$, $(Co(NH_3)_4Cl_2)Cl$ and $(Co(NH_3)_5H_2O)Cl_3$; though in all of these the cobalt atom occurs in the positively electrified portion of the complex molecule.

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[27] *Chem. Berick.*, **45**, 263 (1911).

What is the condition of the atom of the metal in a complex salt? Let us take potassium ferrocyanide as an example, for similar considerations will apply to all the complex salts. In potassium ferrocyanide the iron atom has lost two electrons and is surrounded by 6CN radicles, all of which are negatively electrified. Considerations of symmetry suggest that these negatively electrified radicles are at the corners of an octahedron and the iron atom at the centre. The cyanogen radicles are, using Werner's notation, in the first zone with the atom of iron and are much more closely attached to it than are the atoms of potassium which are in the outer zone. Thus by the close proximity of the negatively charged cyanogens, the atom of iron is exposed to an intense and very symmetrical field of force, and this would (1) give rise to a very strong restoring force; this, if there were no change in the magnetic moments, would until saturation is approached reduce the magnetization. (2) From its symmetry this field tends to make the arrangement of the electrons inside the iron atom more symmetrical and thus reduces the magnetic moment. Both effects occur, the magnetization at ordinary temperature is reduced so much that it is not able to overcome the diamagnetism which iron, like all systems containing electrons, possesses; the number of magnetons is, according to Weiss, reduced to ten, which is only about one-third of the number in an atom of ferric ion. Let us now consider simple salts either in solution or which contain water of crystallization. Since these are electrolytes, the negative constituents of the molecule, such as Cl, SO_4, NO_3, will not be in the inner zone with the iron or other magnetic molecule, but in the outer zone. Thus these negative constituents will exert but little influence on the iron atom, and thus its state and magnetic properties will be but little affected by the change of SO_4 for Cl_2 and so on. The molecules in the zone nearest to the iron atoms are water molecules; these are probably arranged symmetrically around the iron atom and it is also probable that there are six molecules of water in the inner zone. We may picture the atom of iron as at the centre of an octahedron with the water molecules at its corners. As far as the geometrical arrangements are concerned, they are very similar to those of the ferrocyanide with water molecules in place of negatively charged cyanogen radicles. As the water molecules are as a whole uncharged, while the cyanogen ones are negatively charged, we should have expected the field of force to be much stronger with the cyanogen atoms than with the water molecules, so that in the simple salt both the restoring force and the tendency to make the distribution of electrons symmetrical would be less than in the complex salt. Thus both the magnetization and the number of magnetons would be larger for the simple salt than for the complex one. In the salt where iron is trivalent, the iron atom will have lost three electrons; while in the divalent ones, it will only have lost two. Thus there is a difference in the number of electrons in the atoms; this might of itself be supposed to affect the magnetization. In addition to this, since the charge on the trivalent atom of iron is greater than that on the divalent, its attraction on the water molecules will be greater, these will be drawn closer into the atom and will be more favourably situated for influencing the arrangement of the electrons in the atom of iron.

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[28] *Comptes Rendus,* 152, 708 (1911).

In the case of the oxides the conditions are more complicated, we should expect as a general result that in these compounds the closer the connection between the iron and the atoms with which it was combined the lower would be the magnetization and that anything which tended to loosen these bonds would increase the magnetization. A loosening of these bonds would, however, increase the chemical activity of the iron by rendering it easier for it to enter into other combinations, thus we should expect to find correlation between chemical activity and magnetization, a connection which is brought to light very clearly by the experiments of Pascal. From this point of view we can understand a remarkable result obtained long ago by G. Wiedemann, *viz.*, that the magnetic qualities of Fe_2O_3 were increased by mixing with it Al_2O_3; the substances are isomorphous and may combine and form a compound in which the iron is not so firmly bound to other atoms as in Fe_2O_3.

OXYGEN.

The most fascinating of all magnetic bodies is to my mind oxygen. Here we have one of the simplest of atoms; its atom contains only eight electrons, it is a gas, and therefore in the simplest of all physical states, and yet it alone of all gases is paramagnetic and quite strongly so. Another remarkable thing about it is that innumerable as are the compounds of oxygen there is only one, NO, into which oxygen carries its magnetic properties. This would seem to suggest that the magnetic quality does not arise from some quality intrinsic to the atom, but from some speciality in the arrangement of the colligating electrons in those molecules where it exhibits its magnetic character. The oxygen molecule itself is the most conspicuous example; the arrangement of the electrons may be represented symbolically as two cubes having a face in common, this face being at right angles to the line joining the atoms. If the system were rotating about this line there would be an odd number of square faces in rotation. A rotating square with its electrons would act like a current and thus behave like a magneton. Now suppose that the rotation of electrons must be such that adjacent squares rotate in opposite directions, and it is evident that if we start one from rest in one direction, the adjacent one will start in the opposite direction. Suppose then that the electrons in the planes of the squares were rotating so that the rotation in one plane is opposite to that in the adjacent plane, then two of these planes will be rotating in one direction and the third in the opposite, the resulting magnetic effect will be the same as if only one plane rotated, and this will produce a magnet of finite moment.

It might be thought that if this arrangement of electrons were all that is required to produce paramagnetism, a considerable number of gases would be paramagnetic, whereas so far as is known only two possess this property. The consideration of the arrangement of the electrons in gaseous compounds shows, however, that the configuration of O_2 is almost unique in this respect. Consider the arrangement of electrons in some compounds of oxygen, *e.g.*, in water where it is in combination with two monovalent atoms, the electrons are arranged in an octet which has *two* sets of four electrons in parallel planes, if adjacent sets rotate in opposite directions, the total magnetic effect will be zero. The same is true for a compound like CaO, or for one like CO_2, where there are four such sets. We see that whenever the oxygen atom occurs, as it always does in valency compounds, with two additional electrons forming an octet, the effect of one face of the octet will always balance that of the other. In a neutral *atom* of oxygen the electrons would be arranged at the corners of an octahedron; if this were to rotate about one of its axes, the four electrons at right angles to the axis would form an unbalanced system and this would have magnetic properties. The magnetic properties of NO, if we take the arrangement of the electrons to be as that given in the first lecture, would arise from the rotation of the three electrons inside the octet, those on the octet itself would not contribute to the magnetic properties. In the compound C_2H_4 we have a similar arrangement of electrons to those in O_2, but in C_2H_4 all the massive positive charges are not as they are in O_2 on a straight line. The result of this is that if the two octets rotate, say about the line joining the two carbon atoms, they would either have to carry the hydrogen atoms with them, in which case the moment of inertia would be enormously increased, or else move the electrons relative to the hydrogen atoms; the forces between the positive charges and the electrons would resist this motion, and tend to stop the rotation. In the oxygen molecule the electrons can rotate while the positive parts are at rest. If the compounds NCl or NF existed, the arrangement of the electrons would be as in O_2, and on the views we have been expressing we should expect that these compounds would be magnetic.

DIAMAGNETISM.

The diamagnetic properties of chemical compounds will furnish, I think, many searching tests of any theory of the distribution of electrons among the atoms of the compound. According to the theory of diamagnetism given by Langevin,[29] the contribution of an atom to k, the coefficient of diamagnetism, is equal to $\frac{1}{4}\frac{e^2}{m}\Sigma r^2$, where $m\Sigma r^2$ represents the moment of inertia of the electrons in the atom about an axis through their centre of figure. The distribution of electrons is supposed to be quite symmetrical so that the moments about all axes are equal. e is the charge and m the mass of an electron.

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[29] *Annales de Chimie et de Physique* [8], 5, 70 (1905).

If n is the number of atoms per unit volume, k the coefficient of magnetization is given by the equation

$$k = \frac{1}{4} n \frac{e^2}{m} \Sigma r^2 \qquad (32)$$

If M is the molecular weight of the system, $\triangle$ the density of the substance, N the number of hydrogen atoms in a gram of hydrogen

$$n = \frac{\triangle}{M} N \qquad (33)$$

hence

$$\frac{kM}{\triangle} = \frac{1}{4} \frac{e^2}{m} N \Sigma r^2 \qquad (34)$$

Thus $kM/\triangle$, which is called the atomic diamagnetic coefficient and is denoted by χ_a, is proportional to Σr^2, and when χ is known Σr^2 can be calculated. We pass on to consider, what, for our purpose, is the most important application of diamagnetism—the connection between the diamagnetic coefficient of a compound, and those of its constituents.

Pascal[30] has made a series of most valuable experiments on this point, chiefly on organic compounds. He finds that the connection between χ_m, the diamagnetic constant of a compound $A_x B_y C_z$ and χ_a, χ_b, χ_c, the constants for its constituents, is expressed by the relation

$$\chi_m = x\chi_a + y\chi_b + z\chi_c + \lambda. \qquad (35)$$

Where λ is a quantity, generally small compared with χ_a, χ_b, χ_c, which depends on the "bonding" of the atoms. Thus, for example, when oxygen is one of the constituents of the molecule, the value of λ, when the oxygen is connected by two linkages with a carbon atom, is not the same as when the oxygen is connected by one link with a carbon and by another to a hydrogen atom; thus, for example, the contributions of the two oxygen atoms in formic acid HCO.OH are different.

Pascal was dealing with valency compounds; in these, on the electron theory, the atom of any particular element will be associated with the same number of electrons whatever may be the compound in which it occurs; thus, for example, the electronegative elements O, S, F, Cl, will always be surrounded by an octet of electrons; the outer layers of the electropositive elements will have been transferred to the electronegative ones to make up their octets. An interesting point arises here in connection with the hydrogen atom and to a less extent with metal atoms. In a compound of hydrogen with an electronegative element, the electron associated with the hydrogen atom has gone to make up the octet round the negative ion, as, for example, in HCl. Thus the hydrogen atom in such a compound is but a positive core, it has no electrons associated with it, and hence on the electron theory of diamagnetism would not contribute anything to the diamagnetic coefficient. Pascal, however, in deducing the coefficient for any compound, assigns to hydrogen a constant value. This is to some extent a matter of bookkeeping, the electrons transferred from the hydrogen to the chlorine will increase the contribution of the chlorine atom to the diamagnetic coefficient. If we like we may transfer this increase to the credit of the hydrogen atom and regard the hydrogen atom as making a contribution to the diamagnetic coefficient, though it does this not by acting itself as the centre of one of the molecular currents, which account for diamagnetism, but by furnishing an electron which increases the molecular currents in some other atom. We should, however, expect that the amount of the increase would depend upon the kind of atom to which the electron is transferred, that it would increase with the radius of this atom and thus be greater for bromine than for fluorine or chlorine.

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[30] *Annales de Chimie et de Physique* [8], 25, p. 289.

We shall now consider what relation would be indicated on the theory we are considering between the diamagnetism of a compound and of its constituents. On the view that, at any rate, in valency compounds there is a transference of electrons from one atom to another, the atoms in the compound are not in the same state as when they were free and uncombined. The atoms of the electronegative elements such as oxygen or chlorine have gained electrons, while those of the electropositive elements have lost them. The coefficient of diamagnetism is proportional to the sum of the moments of inertia of the electrons about an axis through their centre of figure parallel to the magnetic force. If the transference of the electrons involves a change in this moment the coefficient of diamagnetism will be altered by chemical combination, *i.e.,* the additive law will not hold.

Suppose that in the free state the distances of the electrons from the centres of the atoms of the elements A and B are r_a and r_b, respectively, and that the electrons are symmetrically distributed. Then if there are α electrons on A, β on B the coefficient of diamagnetism is proportional to

$$\frac{2}{3}\alpha r_a^2 + \frac{2}{3}\beta r_b^2 . \tag{36}$$

If, as the result of chemical combination α atoms are transferred from A to B, if R_b is now the distance of the electrons on the B atoms from its centre the coefficient of diamagnetism is now

$$\frac{2}{3}(\alpha + \beta)R_b^2 \tag{37}$$

This may be written in the form

$$\frac{2}{3}\alpha r_a^2 + \frac{2}{3}\beta r_b^2 + \frac{2}{3}\alpha\left(R_b^2 - r_a^2\right) + \frac{2}{3}\beta\left(R_b^2 - r_b^2\right) \tag{38}$$

the sum of the first and second terms is the value given by the additive law, the remaining terms represent corrections which must be applied to obtain the diamagnetic coefficient of the compound. If χ_{AB} represents this coefficient, we see

$$\chi_{AB} = \chi_A + \chi_B + \alpha\lambda_{AB} + \frac{2}{3}\beta\left(R_b^2 - r_b^2\right) \tag{39}$$

when $\lambda_{AB} = \frac{2}{3}(R_b^2 - r_a^2)$ and is a function which involves the dimensions of each of the atoms at the ends of the bond binding them together. The term $\frac{2}{3}\beta(R_b^2 - r_b^2)$ depends only upon the atom B, hence the equation may be written as

$$\chi_{AB} = \chi_A + \chi_B' + \alpha\lambda_{AB} \tag{40}$$

where χ_B' depends only upon the properties of the B atom.

Applying the same reasoning to the most general case, we see that χ the value for the compound $A_xB_yC_z$ will be given by an equation of the form $\chi = x\chi(A) + y\chi(B) + z\chi(C) + \Sigma\lambda_{AB}$.

A term has to be introduced into $\Sigma\lambda_{AB}$ for each electron transferred, *i.e.*, for each valency bond in the compound. Thus we may regard the diamagnetic coefficient of a compound as consisting of a series of terms, one set depending on the atoms in such a way that each atom contributes a definite amount depending only upon the atom; the second set of terms depending on the valency bonds, each bond contributing a term, the value of which depends upon the dimensions of the atoms at the ends of the bond. There may be a term in this set even when the atoms at the ends of the bond are the same; for example, when we have single or double bonds between two carbon atoms: For from the expression for λ we see that they would not vanish unless the radius of the octet round the carbon atoms in the compound C – C was equal to the distance of an electron in a free carbon atom from the centre. As the radius of the octet, round the carbon atoms when there is a double bond C = C is not the same as when there is only a single bond, the value of λ for a double bond is not necessarily twice that for a single one.

Pascal found that a double bond produced a very appreciable *diminution* in the diamagnetism, the magnitude of the effect of the double bond was about equal in magnitude, though opposite in sign to that due to a single carbon atom. The effect of a triple bond was much smaller than that of a double one.

Pascal's researches on the diamagnetism of compounds show that what we have called the λ terms are not in general large compared with the atomic ones, yet these terms undoubtedly exist. He shows, for example, that the contribution of oxygen to the diamagnetic coefficient is not the same, when as in CH_3OH the oxygen is linked by one bond to the carbon and by another to the hydrogen as it is in CH.O.OH, where one of the oxygen atoms is linked by two bonds to the carbon atom; he shows, too, that the contributions of doubly and singly linked carbon atoms are different; he shows in fine that to calculate the diamagnetic coefficient of a compound we must take into account the constitution and configuration as well as the chemical composition.

In addition to the effects produced by the bonding of the atoms, there are others, though probably not so important, arising from what may be called the compressibility of the cell of electrons surrounding the atoms. Thus, for example, it is probable that the distance of the electrons from the centre of the chlorine atoms in HCl is not quite the same as in CCl_4, where the four chlorine atoms may compress each other by their mutual repulsions. A change in the dimensions of the atom would give rise to a change in the diamagnetic coefficient.

The corrections due to the λ terms amount in some cases to as much as 30 per cent., though it is exceptional for them to be as large as this.

From the equation

$$\chi_a = -\frac{1}{4}\frac{e^2}{m} N\Sigma r^2 \qquad (41)$$

we can, if we know the value of χ_a, deduce the distance of the electrons from the centre of the atom. For if the distribution of the electrons in the outer layer is symmetrical about the centre

$$\Sigma r^2 = \frac{2}{3} nR^2 \tag{42}$$

where n is the number of electrons in the outer layer and R the distance of these from the centre of the atom; hence

$$\chi_a = -\frac{1}{6}\frac{e^2}{m} NnR^2 \tag{43}$$

or since $e/m = 1.87 \times 10^7$; $e = 1.6 \times 10^{-20}$; $N = 6.16 \times 10^{23}$

$$\chi_a = -3.06 \times 10^{10} \times R^2 \times n. \tag{44}$$

Pascal[31] gives the following values for $-10^6\ \chi_a$.

H	2.93	Al	13.2	As	43	Te	37.5
Li	4.20	Si	20.0	Sc	23	I	44.6
Bc	8.55	P	26.3	Br	30.5	Cs	41.0
B	7.30	S	15	Rb	27.2	Ba	38.2
C	6.80	Cl	20.1	Sr	24.5	An	45.8
N	5.57	K	18.5	Ag	31	Hg^{ii}	33.4
O	4.61	Ca	15.0	Cd	20	Pt	40.3
F	5.95	Cu	18	In >	15	Pb	45.8
Na	9.2	Lu	13.5	Sn^{iv}	30.3	Bi	192
Mg	10.1	Ga	16.8	Sb^{iii}	74.0		

From these values of χ_a we find from the preceding equation the following values for the diameters of fully charged electronegative atoms. The values found by W. L. Bragg[32] are given for comparison.

Element.	Diameter from Diamagnetic Constant.	Values Found by Bragg.
O	1.02×10^{-8}	1.30×10^{-8}
F	1.05×10^{-8}	1.35×10^{-8}
S	1.84×10^{-8}	2.05×10^{-8}
Cl	2.0×10^{-8}	2.10×10^{-8}
Se	2.23×10^{-8}	2.35×10^{-8}
Br	2.40×10^{-8}	2.38×10^{-8}
Te	2.8×10^{-8}	2.66×10^{-8}
I	3.0×10^{-8}	2.80×10^{-8}

The agreement between the values of the diameters found from the diamagnetic coefficient and those found by Bragg is fairly close. It is interesting to note that there is nothing exceptional in the value of the strongly paramagnetic element oxygen, from this we conclude that the oxygen atom when it has two additional electrons is not paramagnetic.

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[31] *Comptes Rendus,* **158,** p. 1895.

[32] *Phil. Mag.,* **40,** p. 169.

When the diamagnetic substance is in a solid state a somewhat different treatment may be required. If it is a metal, the electrons will be arranged in lattices and along these lattices the electrons may be free to move. If these lattices form a simple cubical system, then it can be shown that the effect of the electrons on the lattices in a plane at right angles to the magnetic force is to produce per unit area of this plane a magnetic moment equal to $-\frac{1}{16}\frac{He^2}{m}$, when H is the magnetic force, if d is the distance between two parallel lattice planes the moment due to the electrons in unit volume is $-\frac{1}{16}\frac{He^2}{md}$, hence the coefficient of diamagnetism is equal to $\frac{1}{16}\frac{e^2}{md}$.

Since the radius of an electron is of the order e^2/m, we see that the volume coefficient of diamagnetism is of the order of the ratio of the radius of the electron to the distance between adjacent atoms.

Since the volume coefficient of diamagnetism varies as l/d, and the atomic volume varies as d^3, we see that for metals of the same valency the diamagnetic coefficient should vary inversely as the cube root of the atomic volume.

CHAPTER V.

ELECTRON THEORY OF SOLIDS.

We shall now proceed to examine how atoms can be bound together not merely in twos or threes to form molecules, but in large numbers so as to form solids. We shall consider how such a collection of atoms is held together and calculate some of its physical properties. We begin with the case when the atoms are all of one kind and when the solid is a crystal, so that it may be regarded as made up of units which are repetitions of each other. These units will be built up of atoms and electrons and the proportion between the number of atoms and the number of electrons will depend upon the valency of the element. Thus for the alkali metals there will be as many atoms as electrons, for the alkaline earths there will be two electrons for each atom, for trivalent metals like aluminum there will be three electrons for each atom and so on. Since the units completely fill space, they must be of the shape of one of the solids into which space may be divided, *i.e.,* the units must be parallelipeda, hexagonal prisms, rhombic dodecahedra or cubo-octahedra.

Let us take the case where the units are cubical. When a number of cubes are built up into a solid each corner of a cube will be the meeting place of eight cubes. Thus, if for purposes of calculation, we take the cube as our unit, and proceed to find the effect of one cube and take the sum of these effects for all the cubes into which the solid is divided, the effect due to an atom or electron at a corner will be counted eight times over. We may compensate for this by assigning to an atom or electron at the corner one-eighth of its normal charge. An atom or electron at the centre of the face of a cube would be common to two cubes and so must be assigned half its normal charge, while an atom or electron at the middle point of a side of a cube will form a part of four cubes and so must be given one-quarter the normal charge.

Thus suppose the atom is at the centre of a cubical layer of electrons, then if the electrons are at the corners of the cube, both electrons and atoms will be arranged in simple cubical lattices, there will be as many electrons as atoms, the unit cell will be a cube with one-eighth of an electron at each corner and an atom at its centre. Suppose the electrons are at the middle points of the faces of the cube as well as at the corners, there will be four electrons for each atom so that the arrangement will be a possible one for a quadrivalent element. The symmetry of the arrangement shows that it corresponds to a crystal in the regular system. The cell in this case will be a cube with one-eighth of an electron at each corner and half an electron at the centre of each face.

Another quite symmetrical arrangement is when there is an electron at the corner of each cube and one at the middle point of each of its twelve sides; as each side is shared by four cubes the twelve electrons at the middle of the sides will only furnish three electrons to the cell, the one-eighth of an electron at each of the corners will contribute another, so that this arrangement would again be representative of an element in which there are four electrons per atom. The cell in this case will be a cube with one-eighth of an electron at each corner, one-quarter of an electron at the middle point of each side and an atom with a charge four at the centre.

The arrangement of the atoms in each of the preceding cases is that of a simple cubical lattice, the experiments of Sir William and Prof. W. L. Bragg on crystal structures have shown that one of the most frequent arrangements of the atoms is that of face-centred cubes. Here the atoms are at the corners and the centres of the faces of the cubes. If such a cube is taken as the unit cell, one-eighth of an atom must be placed at each corner and half an atom at the centre of each face: This makes each cell contain four atoms. If the atom is one of a monovalent element like lithium, the cell must contain four electrons. These electrons can be arranged with cubical symmetry in two ways—

1. By putting one-quarter of an electron at the middle point of each edge and one at the centre of the cube. This gives an arrangement where each atom has six electrons and each electron six atoms for its nearest neighbours. The atoms and electrons are arranged alternately at equal intervals along the lines of a simple cubical lattice.

This arrangement corresponds to that formed by Sir William and Prof. W. L. Bragg for the chlorides of the alkali metals.

2. Put one electron at the centre of four out of the eight cubes into which the unit cube is divided by planes bisecting the sides at right angles. The four cubes are to be chosen as follows:

Take any one and put an electron at its centre, then electrons are to be put at the centres of the three cubes which have an edge but not a face in common with the cube originally chosen. When the cells are put together the same rule must be observed, any two small cubes which have a face in common must have an electron at the centre of one but not at the centre of the other. The four electrons in each cell are at the corners of a regular tetrahedron. The distribution of the atoms and electrons is equivalent to one where each atom is at the centre of a regular tetrahedron of electrons and each electron at the centre of a regular tetrahedron of atoms.

DIVALENT ELEMENTS.

If the atoms in the face-centred cell belong to a divalent element, since there are four atoms in the cell there must be eight electrons.

Two ways in which this may be done are as follows:

1. Fill up the four small cubes which were left empty on scheme 2 for the monovalent elements. Each atom will now have eight electrons as its nearest neighbours, the electrons being at the corners of a cube with the atom at its centre. The cubes surrounding two adjacent atoms have an edge in common and not a face as in the simple cubical arrangement for monovalent atoms.
2. Take the scheme 2 for four of the electrons and in addition place a quarter of an electron at the middle point of each of the twelve sides of the large cube and another electron at its centre.

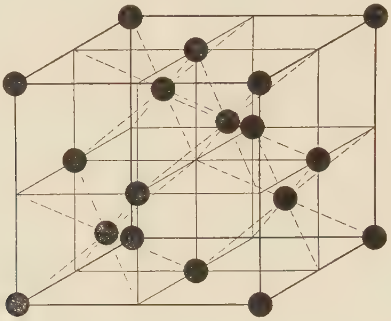
TRIVALENT ATOMS.

When the atoms in the face-centred cube are trivalent there must be twelve electrons in the unit. We can find accommodation for these if we put one at the centre of each of eight small cubes into which the unit cube is divided, a quarter of one at the middle points of each of the twelve edges of the unit cube and another at the centre of this cube. This arrangement is equivalent to putting the atoms at the centres and the electrons at the corners of a series of rhombic dodecahedra filling space.

TETRAVALENT ELEMENT.

The arrangement of the atoms in the diamond has been worked out by the Braggs. It is that shown in Fig. 41. The unit contains eight atoms distributed as follows: One-eighth at each of the corners of the unit, this accounts for one; one-half at the centre of each of the faces, this accounts for three; and four more at the centres of four of the eight cubes into which the unit cube is divided by planes bisecting the sides at right angles. The cubes to be occupied by the atoms are chosen by the same rule as that given for the arrangement of the electrons for the centre-faced arrangement for the monovalent element. As the unit contains eight carbon atoms and carbon is quadrivalent, there must be thirty-two electrons in the unit; these may be arranged as follows:

Fig. 41.



(*a*) At the middle points of the sides of the cubical unit; this accounts for three.

(*b*) At the centre of each of the faces of the eight small cubes; this accounts for twenty-four.

(*c*) At the centres of the four small cubes not occupied by the carbon atoms; this accounts for four.

(*d*) One at the centre of the large cube.

Röntgen-ray analysis has shown that for some elements the atoms are arranged at the corners and the centre of a cube. Taking this cube as the unit it contains two atoms; if the element is monovalent, it must contain two electrons. We cannot place these electrons so as to get complete cubical symmetry for one such unit; if, however, we group eight such units together, we get a larger cubical unit containing sixteen atoms, and it is possible to arrange sixteen electrons in this larger unit so as to get cubical symmetry. Thus we might put pairs of electrons along the diagonals of the eight cubes which go to make up the larger unit.

If the atom were a divalent one we should have to accommodate four electrons in the original unit. This may be done by putting them at the centres of four out of the eight cubes into which the unit may be divided.

HEXAGONAL SYSTEM.

We have hitherto confined ourselves to the consideration of crystals in which the unit was a cube and the arrangement both of atoms and electrons completely symmetrical, so that the crystals would belong to the regular system. If our unit were a hexagonal prism, if, for instance, the electrons were at the corners and the atoms at the centres of hexagonal prisms, then since each corner is common to six prisms, we must, when calculating the electrical forces due to the unit, give to each electron at the corner one-sixth of its normal charge, the twelve electrons at the corners are thus equivalent to two electrons, so that the unit contains two electrons for each atom and would thus correspond to a divalent element.

The arrangement of electrons and atoms in the systems we have described have such regularity that the calculation of the properties of such an aggregate is easier than that of the properties of an aggregate of a small number of atoms in an individual molecule. For the electrons in one part of a molecule, for example, those at the ends of the two octets which form the oxygen molecule, are exposed to forces which are different from those acting on the electrons between the two oxygen atoms. The greater regularity in the arrangement of the electrons in the crystal more than compensates, as far as the mathematical difficulties are concerned, for the necessity of taking into account the effect of a much larger number of electrons and atoms than is necessary for the molecule.

I have in a paper published in the *Philosophical Magazine* (53, p. 721) calculated some of the properties of crystals when the atoms and electrons are arranged according to some of the schemes we have just been discussing. I shall describe the results of these investigations, beginning with the simplest case, where the atoms and electrons are both arranged in simple cubical lattices, where each atom may be regarded as the centre of a cube formed by eight electrons.

In the paper referred to, the stability of the system is investigated, and it is shown that if $2d$ is the distance between two atoms the arrangement will be stable, provided d is less than $c/1.69$ where c is the distance at which the force exerted by the positive nucleus on an electron changes from attraction to repulsion. As the distance between an atom and the nearest electron is $\sqrt{3}d$, *i.e.*, $1.72d$, we see that for the equilibrium to be stable, the shortest distance between an atom and an electron in the solid cannot exceed by more than a very small amount the distance of the electron from the centre of the atom when the element is in the gaseous state.

The system of electrons and atoms in the metal will have a very large number of periods of vibration, depending on the way the electrons are displaced relatively to each other and to the atoms; the highest frequency of these vibrations is when the electrons are not displaced relatively to each other, but only with respect to the atoms; this corresponds to the displacement which would be produced by light whose wave-length is long compared with the distance between two atoms. I find that this maximum frequency, p, is given by the equation

$$mp^2 = .384\, ce^2/d^4 \qquad (45)$$

where m is the mass and e the charge on an electron.

If M is the mass of an atom and $\triangle$ the density of the solid, then since $8d^3$ is the volume of a cell, $1/8d^3$ is the number of cells in a cubic centimetre, hence

$$\frac{M}{8d^3} = \triangle \qquad (46)$$

so that equation (45) may be written as

$$mp^2 = .384\, e^2 \frac{8\triangle}{M} \frac{c}{d} \qquad (47)$$

This type of vibration is the one that would be excited by waves such as those of visible or ultra-violet light whose wave-length is large compared with the distance between the atoms in the solid. We might therefore expect evidence of it in the behaviour of monovalent metals when acted upon by light, the effect produced upon such metals would be greatest when the frequency of the incident light was that given by equation (45). An interesting case when the action of light on a metal is a maximum for light of a particular wave-length is what is known as the selective photoelectric effect.[33] This has been measured by

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[33] Hughes, "Photoelectricity," Chap. 5.

Pohl and Pringsheim,[34] and in the following table, I give the comparison of the wave-length λ for which the selective photoelectric effect is a maximum for the monovalent metals sodium, potassium and rubidium as determined by Pohl and Pringsheim with the wave-lengths calculated by equation (45) where c/d has been given the value 1.7, *i.e.*, on the supposition that the shortest distance between the atom and the electron in the metal is the same as that in the gas.

Metal.	Δ	$M/1.64 \times 10^{-24}$	λ calculated.	λ observed.
Sodium	.971	23	3234	3400
Potassium	.862	39	4457	4400
Rubidium	1.532	85.45	4940	4800

It will be noticed that the agreement between the observed and calculated values is satisfactory.

It is interesting to compare the frequency of this type of vibration of the electrons in the solid, with P, that of the vibration of the electron in a gaseous atom, the latter can easily be proved to be given by the equation

$$mP^2 = e^2/c^3 \tag{48}$$

so we see from (45) if $1.7d = c$ and p is the frequency in the metal

$$p = 1.8P \tag{49}$$

thus the frequency in the metal is a little less than twice that in the gas, the values for the wave-length of the vibrations in the gaseous atom deduced from the table just given are for sodium 5800, and for potassium 7900.

The slowest vibrations of the electrons are when the displacement of adjacent electrons are in opposite directions. Thus suppose one of the lines of the electron lattice is vertical, then the slowest vibration of the electrons is when the electrons in any one line have all equal vertical displacements and the displacements of the electrons in the six vertical lines which are its nearest neighbours are equal in magnitude, but opposite in direction, to that in the line under consideration.

COMPRESSIBILITY OF THE METALS.

We can calculate the potential energy due to the forces between the atoms and the electrons. I have given the calculations in a paper in the *Philosophical Magazine* (43, p. 721) and have shown that if the metal is supposed to be made up of cubical cells with an atom at the centre and one-eighth of an electron at each of its eight corners, each cell corresponding to an atom with its electron, the potential energy per cell is

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[34] *Verh. d. Deutsch. Phys. Gesell.*, 13, p. 474 (1911).

$$-1.825\frac{e^2}{2d} \tag{50}$$

when $2d$ is a side of the cube. Thus, if there are N cells per unit volume, the potential energy per unit volume is

$$-1.825\frac{e^2}{2d}N \tag{51}$$

Now $N=1/8d^3$, and if as before M is the mass of an atom and Δ the density of the metal

$$NM=\Delta \tag{52}$$

hence the potential energy per unit volume is equal to

$$-1.825\,e^2\left(\frac{\Delta}{M}\right)^{\frac{4}{3}} \tag{53}$$

It is shown also that the work required to compress the cells so that the distance between two atoms is reduced from $2d$ to $2(d-\Delta d)$ is equal to

$$1.825\frac{Ne^2}{2d}\left(\frac{\Delta d}{d}\right)^2 \tag{54}$$

If dV is the diminution in a volume V due to this diminution in d

$$\frac{dV}{V}=3\frac{\Delta d}{d} \tag{55}$$

hence the work required to compress the cells in unit volume is equal to

$$\begin{aligned}&\frac{1.825}{9}\frac{N}{2d}e^2\left(\frac{dV}{V}\right)^2\\ &=\frac{1.825}{9}e^2\left(\frac{\Delta}{M}\right)^{\frac{4}{3}}\left(\frac{dV}{V}\right)^2\end{aligned} \tag{56}$$

But if k is the bulk modulus, then this work is equal to

$$\frac{1}{2}k\left(\frac{dV}{V}\right)^2 \tag{57}$$

hence

$$k=\frac{3.65}{9}e^2\left(\frac{\Delta}{M}\right)^{\frac{4}{3}} \tag{58}$$

The "compressibility" of the substance is equal to $1/k$.

We owe to Professor Richards invaluable determinations of the compressibility of the various elements. The following table contains the results of the comparison of his values of the compressibility with those calculated from equation (58).

Metal.	$\triangle$	$M/1.64 \times 10^{-24}$.	k calculated.	k observed.
Lithium	.534	7	$.14 \times 10^{12}$	$.114 \times 10^{12}$
Sodium	.971	23	$.068 \times 10^{12}$	$.065 \times 10^{12}$
Potassium	.862	37	$.03 \times 10^{12}$	$.032 \times 10^{12}$
Rubidium	1.532	85.5	$.022 \times 10^{12}$	$.025 \times 10^{12}$
Cæsium	1.87	132	$.016 \times 10^{12}$	$.016 \times 10^{12}$

Thus the results given by equation (58) are in close agreement with experiment.

If the atoms are in the gaseous state, the work required to change the radius of an atom from r to $r - \triangle r$ is equal to $\frac{1}{2} \frac{e^2}{c} \left(\frac{\triangle r}{r}\right)^2$. Thus to produce the same percentage changes (45) in the sum of the volume of the atoms when in the gaseous state and (47) in the volume of the same number of atoms in the solid state requires the expenditure of amounts of work which are in the proportion of $\frac{1}{c}$ to $\frac{1.825}{d}$, or if $1.7d = c$, of 1 to 3.1. Thus the compressibility of the atoms in the solid state is about one-third of that in the gaseous.

The potential energy of a cell in the solid is equal to $\frac{-1.825 e^2}{2d}$ or, since $\frac{1}{(2d)^3} = \triangle / M$, to $-e^2 \, 1.825 \left(\frac{\triangle}{M}\right)^{\frac{1}{3}}$; if M' is the atomic weight of the element

$$M = 1.64 \times 10^{-24} \times M' \qquad (59)$$

hence the potential energy of the metal per cell is equal to

$$-e^2 \, 1.5 \times 10^8 \left(\frac{\triangle}{M'}\right)^{\frac{1}{3}} \qquad (60)$$

This is equal to the energy acquired by the charge on an electron falling through a potential difference of

$$21.25 \times \left(\frac{\triangle}{M'}\right)^{\frac{1}{3}} \text{ volts.} \qquad (61)$$

The values for the various alkaline metals are

Li = 9.25 volts
Na = 7.3
K = 6.36
Rb = 5.52
Cs = 5.100

The work which must be done to pull the cell from the metal and convert it into an atom of a monatomic gas is the difference between the potential energy in the cell and the potential energy of the gaseous atom; the latter when expressed in volts is for a monovalent element equal to the ionising potential.

The potential energy per cell is equal to $-\frac{1}{2}(w_1 + w_2)$ where w_1 is the work required to remove a single electron from the metal and w_2 that required to remove a single atom. We have calculated $w_1 + w_2$, but not w_1 and w_2 individually. If the repulsion between the positive parts of two atoms was proportional to the inverse square of the distance, then w_1 would be equal to w_2, but if the repulsion is equal to $\frac{e^2}{r^2}\left(1 - \frac{cp}{r}\right)$, then w_2 will be greater than w_1, and w_1 will be less than $\frac{1}{2}(w_1 + w_2)$. Let $w_1 = \frac{\beta}{2}(w_1 + w_2)$ where β is a fraction, then the work required to remove any electron from the alkali metals will be β times the values given in the preceding tables. The contact difference of potential between two metals is equal to the difference in the amounts of work required to remove an electron from the two metals, thus the contact difference of potential between sodium and potassium would be $\beta(7.3 - 6.36) = .92\,\beta$ volts. The value found by experiment is .4 volt, hence $\beta = .44$, so that $w_1 = .44$ (potential energy per cell).

This gives the following values for the work required to tear an electron from the alkali metals.

Li = 4.07 volts
Na = 3.2
K = 2.79
Rb = 2.42
Cs = 2.24

The work required to tear an electron from sodium was estimated by Richardson from thermionic data as 2.6 volts, and from the photoelectric effect as 2.1 volts. The values given in the table represent the work required to remove an electron from the *body* of the metal; the atoms in the surface layers of the metal differ in energy from those in the interior, and an electron can escape from them with less expenditure of energy. As the values given in the table are less than half the amount of work required to remove both an electron and the positive part of an atom from the metal, the work required to remove an atom is greater than that required to remove an electron, so that when the metal is heated, the number of positive ions which come off will be small compared with the number of electrons.

The values given on page 120 for the compressibility are for a distribution of atoms and electrons such that the atoms are at the centres of cubes and the electrons at the corners.

When the atoms and electrons are arranged so that atoms and electrons occur alternately at equal intervals along the lines of a cubical lattice, we can show that the potential energy for a volume of the metal containing N electrons and N atoms is

$$-1\cdot77\frac{Ne^2}{2d} \tag{62}$$

where d is the shortest distance between an atom and an electron. If these N atoms and electrons make up unit volume, then if $\triangle$ is the density of the metal and M the mass of an atom, since a cube with side $2d$ contains four atoms

$$\begin{aligned}\frac{4M}{8d^3} &= \triangle: \quad NM = \triangle\\ \frac{1}{d} &= \left(\frac{2\triangle}{M}\right)^{\frac{1}{3}}\end{aligned} \tag{63}$$

hence the potential energy per unit volume is

$$\begin{aligned}&-.885\, e^2\, 2^{\frac{1}{3}}\left(\frac{\triangle}{M}\right)^{\frac{4}{3}}\\ &= -1.1e^2\left(\frac{\triangle}{M}\right)^{\frac{4}{3}}\end{aligned} \tag{64}$$

It follows from this that the bulk modulus is

$$\frac{2.2e^2}{9}\left(\frac{\triangle}{M}\right)^{\frac{4}{3}}, \tag{65}$$

this is not very much more than half the value $\frac{3\cdot65\,e^2}{9}\left(\frac{\triangle}{M}\right)^{\frac{4}{3}}$ corresponding to the other distribution which we saw agreed very well with the experiment results; hence we conclude that the atoms and electrons cannot in the alkali metal be arranged so as to occur alternately at equal intervals along the lines of a cubical lattice.

For the arrangement where the atoms are arranged in face-centred cubes with electrons at the centres of four out of the eight smaller cubes into which the face-centred cube is divided, I find that the potential energy for a volume containing N atoms and N electrons is

$$-1\cdot75\left(\frac{\triangle}{M}\right)^{\frac{4}{3}} \tag{66}$$

so that k, the bulk modulus, is equal to

$$\frac{-3\cdot50}{9}e^2\left(\frac{\triangle}{M}\right)^{\frac{4}{3}} \tag{67}$$

this differs by less than 5 per cent. from the value given by equation (58), and would agree within the errors of experiments with the values found by Richards.

When the arrangement of the atoms of a monovalent element is that of the body-centred cube and the electrons are placed two by two along the diagonals of eight such cubes taken as a single unit, Miss Woodward finds

$$k = \frac{3{\cdot}2}{9} e^2 \left(\frac{\Delta}{M}\right)^{\frac{4}{3}} \tag{68}$$

This would give values for k appreciably smaller than those found by experiment. The arrangement of the electrons was assumed to be as follows: Two electrons were placed inside each cube on a diagonal, one on one side of the centre, the other on the other, midway between the centre of the cube and the ends of the diagonal. The diagonals along which the electrons are placed are chosen so that in a cube built up of eight such small cubes no two of the diagonals in any four whose centres are in one plane are parallel or intersect. The diagonals in two cubes which have a corner but neither an edge nor a face in common are to be parallel. This arrangement is equivalent to arranging the atoms and electrons alternately at equal intervals along lines whose directions are parallel to the four diagonals of the cube.

THE ENERGY AND COMPRESSIBILITY OF DIVALENT ELEMENTS.

We shall further test the electron theory of solids by calculating the compressibility of a divalent element. Calcium crystallises in the regular system and the arrangement of the atoms has been shown by X-ray analysis to be that of the face-centred cube. Taking such a cube as the unit, it contains four calcium atoms; since calcium is divalent, if there are four atoms there must be eight electrons. The most symmetrical way of arranging these is to place one at the centre of each of the eight small cubes into which the unit cube is divided by planes bisecting its sides at right angles.

Taking this arrangement, I find that the electrostatic potential energy of a calcium atom is, if $2d$ is a side of the unit cube,

$$-\frac{e^2}{d} 5{\cdot}33 \tag{69}$$

while that of an electron is equal to

$$-\frac{e^2}{d} 1.8 \tag{70}$$

Hence the electrostatic potential energy of one atom and two electrons is

$$-\frac{e^2}{d}\,8.93 \qquad (71)$$

The total actual potential energy, *i.e.*, the potential energy when we take into account the effect of the forces varying inversely as the cube of the distance is one-half of this, *i.e.*,

$$-\frac{e^2}{d}\,4.46 \qquad (72$$

Since the cube whose volume is $8d^3$ contains four atoms

$$\frac{4M}{8d^3} = \triangle \qquad (73)$$

where M is the mass of an atom and $\triangle$ the density of the metal; hence the energy per unit volume is equal to

$$-e^2\,5.61 \times \left(\frac{\triangle}{M}\right)^{\frac{4}{3}} \qquad (74$$

The bulk modulus k is equal to

$$e^2\,\frac{11.2}{9}\left(\frac{\triangle}{M}\right)^{\frac{4}{3}} \qquad (75)$$

for calcium $\triangle = 1.55$ and $M = 40 \times 1.64 \times 10^{-24}$, hence k for calcium $= .192 \times 10^{12}$. The compressibility which is the reciprocal of k is 5.2×10^{-12}; the value found by Richards is 5.5×10^{-12}, so that the agreement between the observed and calculated values is quite satisfactory.

The potential energy for an atom and two electrons is that corresponding to the fall of an electron through twenty-two volts.

THE COMPRESSIBILITY OF A TRIVALENT ELEMENT.

Aluminum is a trivalent element crystallising in the regular system. The arrangement of the atom has been shown to be that of a face-centred cube. Taking this cube as the unit it contains four atoms; it must, therefore, since aluminum is trivalent, contain twelve electrons. If we place electrons at the middle points of the sides, at the centres of each of the eight cubes into which the unit cube is divided by bisecting planes and one at the centre of the cube, we get a symmetrical distribution of these twelve electrons. This distribution is the same as if each atom were placed at the centre of a rhombic dodecahedron and the electrons at the corners of the dodecahedron. Since four planes meet at some of the corners while only three meet at others, we see that the electrons will be divided into two groups.

For this arrangement I find that the electrostatic potential energy of the atom, with its triple charge of electricity, is equal to

$$-e^2\,\frac{10.6}{d} \tag{76}$$

where $2d$ is the side of the face-centred cube and e the charge on an electron.

For an electron at a corner of the dodecahedron where four planes meet, the potential energy is

$$-e^2\,\frac{.05}{d} \tag{77}$$

and for an electron at a corner where three planes meet

$$-e^2\,\frac{1.75}{d} \tag{78}$$

Each atom is associated with one electron of the first type and two of the second, hence the electrostatic potential energy of this system is $-e^2\frac{14.25}{d}$ and the total potential energy $-e^2\frac{7.12}{d}$.

Now

$$\frac{1}{d}=\left(\frac{2\triangle}{M}\right)^{\frac{1}{3}} \tag{79}$$

hence k the bulk modulus is given by the equation

$$k=\frac{17.8}{9}\,e^2\left(\frac{\triangle}{M}\right)^{\frac{4}{3}} \tag{80}$$

for aluminum $\triangle = 2.65$, $M = 27 \times 1.64 \times 10^{-24}$; hence $k = 1.08 \times 10^{12}$, the value found by experiment is $.78 \times 10^{12}$.

COMPRESSIBILITY OF THE DIAMOND.

In the diamond we have a quadrivalent element crystallising in the regular system. The arrangement of the carbon atoms in the diamond has been shown by Sir W. H. Bragg and Prof. W. L. Bragg to be given by the following scheme. The atoms occupy

(*a*) the corners of a cube;
(*b*) the centres of its faces;
(*c*) four of the centres of the eight cubes into which the large cube is divided by planes bisecting its sides at right angles.

We shall take this cube as our unit; it contains eight carbon atoms. Since carbon is quadrivalent, it must contain thirty-two electrons; these electrons will be situated

(*a*) at the middle points of the edges of the cubical unit; this accounts for three;

(*b*) at the centres of each of the faces of the eight small cubes; this accounts for twenty-four;

(*c*) at the centres of the four small cubes not occupied by the carbon atoms; this accounts for four;

(*d*) one at the centre of the large cube.

Making use of this unit, we can calculate the electrostatic potential energy due to the charges on the atoms and electrons. Let E be the charge on a carbon atom, e that on an electron.

The electrostatic potential energy of a carbon atom

$$\frac{1}{2}E\left(\frac{\Sigma e}{r'}-\frac{\Sigma E}{r}\right) \tag{81}$$

I find to be equal to

$$\frac{1}{2}\frac{E}{d}(149.346e-35.13E), \tag{82}$$

where $2d$ is the side of a unit cube. Since $E=4e$, this reduces to

$$17.65\frac{e^2}{d}. \tag{83}$$

The electrostatic potential energy of an electron I find to be

$$\begin{aligned}\frac{1}{2}\frac{e}{d}\left\{\frac{E}{4}\,149.346-147.59e\right\}\\ =\frac{1}{2}\frac{e^2}{d}1.75.\end{aligned} \tag{84}$$

Hence the electrostatic potential energy for the atom and its four associated electrons is $21.15\,\frac{e^2}{d}$.

Since there are eight atoms in the cube whose edge is $2d$, if $\triangle$ is the density of the diamond and M the mass of a carbon atom,

$$\frac{8M}{8d^3}=\triangle \tag{85}$$

or

$$\frac{1}{d}=\left(\frac{\triangle}{M}\right)^{\frac{1}{3}}. \tag{86}$$

Thus the electrostatic potential energy per one atom and four electrons is

$$21.15e^2\left(\frac{\triangle}{M}\right)^{\frac{1}{3}}, \tag{87}$$

and the energy per unit volume is

$$21.15e^2\left(\frac{\triangle}{M}\right)^{\frac{4}{3}}. \tag{88}$$

Hence k, the bulk modulus of the diamond, is given by the equation

$$k=\frac{21.15}{9}e^2\left(\frac{\triangle}{M}\right)^{\frac{4}{3}}; \tag{89}$$

for the diamond $\Delta = 3.52$, $M = 12 \times 1.64 \times 10^{-24}$; hence $k = 5.6 \times 10^{12}$, $1/k = .178 \times 10^{-12}$.

This value for $1/k$ is much less than that, $.5 \times 10^{-12}$, found by Richards. It is, however, in close agreement with $.16 \times 10^{-12}$, the value recently found by Adams.[35]

The properties of solids formed by elements whose atoms have more than four disposable electrons are quite different from those of solids formed by the elements with one, two, or three disposable electrons. The latter are, with the exception of boron, metallic and good conductors of electricity and heat. The former, for instance sulphur and phosphorus, are insulators. Not only do they insulate in the solid state, but they do so after they are fused. They differ in this respect from solid salts which, though they may insulate when in the solid state, generally conduct when melted. This suggests that in the salts there are positively and negatively electrified systems which are fixed when the substance is in the solid state, but can move about when it is liquefied. In such elements as sulphur or phosphorus there does not seem to be any evidence of the existence of anything but neutral systems; in other words, the solid may be regarded as built up of units, each of which contains as much positive as negative electricity. It is noteworthy that according to the Electron Theory of Chemical Combination, two similar atoms, if they have each more than four disposable electrons, like the atoms of sulphur and phosphorus, can combine and form a saturated molecule, which is electrically neutral.

Thus we are led to distinguish three types of solids:

(*a*) A type where the atoms are arranged in lattices, and the electrons in other lattices coördinated with the atomic ones. In this type each electron has no closer connection with a particular atom than it has with several others. Thus, for example, when the electrons form a simple cubical lattice with the atoms at the centres of the cubes, each electron has eight atoms as equally near neighbours; so that an electron is not bound to a particular atom. This type includes the metals; it also includes boron and carbon in the form of diamond, which are insulators.

(*b*) A type represented by the salts; here the atoms are again arranged in lattices, but each electron has much closer relation with one particular atom than it has with any other. Thus to take the case of NaCl, where the Braggs have shown the atoms to be arranged according to the following scheme:

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[35] *Washington Acad. Sc.*, 11, p. 45 (1921).

Na	Cl	Na	Cl
Cl	Na	Cl	Na
Na	Cl	Na	Cl

We suppose that each sodium atom has lost an electron, while each chlorine atom has gained one; thus each chlorine atom has eight electrons around it, and each electron is much more closely bound to one particular chlorine atom than to any other. It is so closely associated that it is not dissociated from its partner in either the solid or liquid state of the substance. Thus the chlorine system always has a negative charge, the sodium one a positive. These atoms do not move when the substance is in a solid state, though they may do so when it is liquefied.

If the distance of the electrons from the chlorine atoms were to increase until it was not far from half the distance between the sodium and chlorine nuclei, this type would approximate to type (*a*).

(*c*) A type where the lattices are built up of units which are not electrified; such units are probably molecules containing two or more atoms, though in certain cases they may be single atoms. The characteristic of the type is that each unit has sufficient electrons bound to it to make it electrically neutral, and that each electron remains attached to a particular atom. Thus where an electric force acts on the system there is no tendency to make the unit move in one direction rather than the opposite, so that the substance cannot conduct electricity.

There is something anomalous about the compressibility of silicon; the arrangement of its atoms as determined by X-ray analysis is the same as that of the diamond, while its atomic volume is 2.7 times greater. We might therefore expect that its compressibility would be $(2.7)^{\frac{4}{3}}$, or 3.8 times that of the diamond. Its compressibility, however, as determined by Richards, is only $.16 \times 10^{12}$, which is practically the same as the revised value for the diamond. In silicon, however, there are two layers of electrons so that when the four electrons in the outer layer have been distributed to form the lattice, a layer of eight will remain surrounding the positive part of the atom. The compression of the silicon may involve not merely the closer approach of the positive parts of the silicon atoms, but also a closer approach to the central atom of the layer of eight electrons which surround it. The work required to do this would tend to make the compressibility less than for a substance like carbon, which, after its outer layer has been distributed, has no inner layer left to compress.

TABLE VIII.

Potential Energy per Atom with Its Associated Electrons.

Arrangement of Atoms.	K. (Bulk Modulus).
Monovalent Elements.	
CUBICAL	$\frac{3.65\,e^2}{9}\left(\frac{\Delta}{M}\right)^{\frac{4}{3}}$
FACE-CENTRED CUBE:	
Electrons at middle points of edges and centre of cube	$\frac{2.2\,e^2}{9}\left(\frac{\Delta}{M}\right)^{\frac{4}{3}}$
Electrons at centres of four constituent cubes	$\frac{3.5\,e^2}{9}\left(\frac{\Delta}{M}\right)^{\frac{4}{3}}$
BODY-CENTRED CUBE	$\frac{3.2e^2}{9}\left(\frac{\Delta}{M}\right)^{\frac{4}{3}}$
Divalent Elements.	
FACE-CENTRED CUBE:	
Electrons at centres of eight constituent cubes	$\frac{11.2\,e^2}{9}\left(\frac{\Delta}{M}\right)^{\frac{4}{3}}$
Electrons at centres of edges and four constituent cubes	$\frac{7.75\,e^2}{9}\left(\frac{\Delta}{M}\right)^{\frac{4}{3}}$
Trivalent Elements.	
FACE-CENTRED CUBE:	
Electrons at middle points of edges and centre of cube and at centres of four constituent cubes	$\frac{18\,e^2}{9}\left(\frac{\Delta}{M}\right)^{\frac{4}{3}}$
Quadrivalent Elements.	
FACE-CENTRED CUBE and at:	
Centres of four constituent cubes. Electrons, centres of edges, centres of faces of constituent cubes and at centres of four of these cubes	$\frac{21.15\,e^2}{9}\left(\frac{\Delta}{M}\right)^{\frac{4}{3}}$

The case may be compared with that of a chloride of an alkali metal, say LiCl. In the lattice formed by the atoms each chlorine atom is surrounded by a layer of eight electrons. The compressibility of the salt has been determined by Richards and it is much less than the value calculated on the supposition that the chlorine ion with its octet of electrons round a positive charge of seven units can be treated as a negative charge of one unit at the centre of the chlorine atom. The compression of the octet round the chlorine atom has also to be taken into account. Miss Woodward has done this recently and finds that the calculated values are in fair agreement with those determined by experiment.

A similar argument applies to the elements copper, silver and gold, which are far less compressible after allowing for the difference in the atomic volume than they would be if they followed the same law as the other monovalent elements, the alkali metals. The heavier alkali metals have also inner layers, but the atomic volume of these is so great that the compression of these layers does not come nearly so much into play as in gold and silver, which have much smaller atomic volumes.

We may sum up the results of the preceding investigation of the compressibility of solids as follows:

The compressibility is equal to $C\left(\frac{\triangle}{M}\right)^{\frac{4}{3}}$, where C is a quantity depending on the valency of the element and the form in which it crystallises; $\triangle$ is the density of the solid and M the mass of an atom of the element.

The potential energy of an atom with its associated electrons is equal to

$$-\frac{4\cdot 5}{C}\left(\frac{\triangle}{M}\right)^{\frac{1}{3}} \qquad (90)$$

Table VIII contains a summary of the preceding results.

SURFACE TENSION.

The preceding expression represents the energy of an atom in the mass of the metal, for one on the surface it requires modification. Thus if P is an atom or electron part of its potential energy depends on the atoms and electrons above a horizontal plane through P. If the metal is broken so that this plane becomes a surface of the metal, the atoms and electrons above P will no longer affect the potential energy so that this will be changed. We can find an approximation to the amount of this change in the following way: Let us take a crystal of a monovalent element and suppose that the atoms and electrons are arranged in the plane of the surface according to the scheme (1, p. 114) when the atoms are at the corners and centres of the faces of a cube and the electrons at the middle points of the sides and the centre of the cube. This is the more convenient arrangement to take, since the atoms and electrons are present in equal numbers in the plane, so that the total electric charge upon it is zero. With this arrangement I find that the contribution of the atoms and electrons above P to the potential energy of the system consisting of P and an electron is $-.075\frac{e^2}{d}$, where d is the distance between an atom and the nearest electron. We saw (p. 122) that in this case for an atom and electron in the interior the energy is $-1.77\frac{e^2}{d}$. Thus the potential energy S of the atom and electron in the surfaces exceeds I, the potential energy in the interior, by $\frac{.075}{1.77}I = .042\,I$. The surface tension arises from the excess of the potential energy of the atoms in the surface over those in the interior and is equal to the excess for one atom multiplied by the number of atoms in unit area of the surface. Let us apply this to find the surface tension of sodium. The energy of an atom of sodium not on the surface is equal to that gained by an electron falling through 7.2 volts, *i.e.,* $7.2 \times 1.6 \times 10^{-12}$ ergs. The distance between two sodium atoms is equal to 3.37×10^{-8}, hence the number of sodium atoms per square centimetre is $10^{16}/11.35$. Thus the surface tension of sodium is

$$\begin{aligned} &.042 \times 7.2 \times 1.6 \times 10^4/11.35 \\ &= 432 \text{ ergs/cm.}^2 \end{aligned} \qquad (91)$$

The value given in the tables for molten sodium is 500, so that the calculated and the observed value are of the same order of magnitude. The calculation is only a rough approximation as we have neglected the effect of temperature and supposed that the distance between the sodium atoms is the same on the surface as in the interior. The increase in the potential energy at a surface will depend upon the orientation of the surface. Thus if the face of the sodium is a plane parallel to the diagonal plane of the cube instead of the plane parallel to one of its faces, I find that the potential energy of an atom and electron at the surface will be greater than if they were in the interior by $.067\,I$ instead of $.0423\,I$ as in the former case. In this plane the number of atoms per unit area is only $1/\sqrt{2}$ that in the former case, thus the surface tension in this plane will be to that in a plane parallel to a face of the cube in the proportion of 47.3 to 42. The atoms in this plane having greater potential energy than those in a plane parallel to the faces of the cube will develop a greater amount of heat when they enter into chemical combination. I find that for a gram molecule of sodium the difference would be about 10,000 calories. Thus chemical action would be more likely to go on at these faces than at the natural cleavage faces of the crystal; the photoelectric emission of electrons would also be greater.

COMMUNICATION OF A CHARGE FROM GASEOUS IONS TO THE ELECTRODES.

The preceding values have an important bearing on the transmission of electric charges from gaseous ions to metallic electrodes.

Consider first the case of a positively charged ion. If this is to give up the charge to the electrode and escape as an uncharged atom or molecule, an electron must come from the metal, and be received by the ion. Let the work required to abstract the electron from the metal be V_m and let the ionising potential of the gas be V_g, then the work required to discharge the ion is $V_m - V_g$. If V_m is greater than V_g it will require an expenditure of work to discharge the ion, the ion will not give up its charge, *i.e.*, there will be no continuous current through the gas unless the external potential difference is greater than $V_m - V_g$.

Now take the case of a negatively electrified ion giving up its charge to the anode; here an electron has to be taken from the ion and given up to the anode; to remove the electron requires an amount of energy equal to V_1, where V_1 is the work required to move an electron from the negatively charged ion, it will be less than the ionising potential. On the other hand, work equal to V_m is gained when the electron goes into the metal thus to effect the transference, work equal to $V_1 - V_m$ must be done, so there must be an external potential difference greater than $V_1 - V_m$ to keep up the current.

Though the ionising potential for an atom is in general much greater than the work required to extract an electron from a metallic electrode, yet if the ions are not single atoms but are hydrated or form part of an aggregate, the work gained by the fall of an electron into the ion will, as is explained on page 76, be much less than that corresponding to the ionising potential of the atom. If this work sinks below V_m a finite potential difference will be required to make these hydrated positive ions give up their charges to the cathode.

On the other hand, the work required to extract an electron from a hydrated negative ion will be greater than that which would be required if the ion were not hydrated, if this work exceeds V_m a finite potential difference will be required to make these negative ions give up their charge to the anode.

INTERMETALLIC COMPOUNDS.

The expression we have found for the potential energy of a solid has an important application to the theory of intermetallic compounds and alloys. Take the case of two metals, *A* and *B*, when they are apart they consist of lattices of atoms and electrons, and as we have seen may be regarded as built up of units, each unit containing a certain number of atoms, together with the appropriate number of electrons. Thus if the metal were monovalent there would be as many electrons as atoms; if it were divalent there would be twice as many, and so on. Suppose now that the metals were mixed under conditions which permitted free movement of the atoms and electrons. Then in the mixture in addition to the units consisting wholly of *A* or of *B* atoms, we may have units containing both *A* and *B* atoms. Thus to take a definite case, let *A* be sodium and *B* potassium, the unit might be a cube of side *2d*, built up of eight cubes; at the centres of these, atoms of sodium and potassium might be placed alternately, the electrons would be at the corners, the centres of the faces, and the centres of the edges, and at the centre of the large cube. Such a unit would certainly be formed at low temperatures if its potential energy were less than that due to four units of sodium and four of potassium when these metals were separated. Again we might have a cubical unit with the potassium atoms at the corners and the sodium atoms at the centres of the faces; in this unit there would be three sodium to one potassium atom. There are many other possible units with different proportions of sodium and potassium atoms. Whether such units will be formed or not is a question of the relation between the potential energy of such a unit and the potential energy of the atoms it contains when arranged so that the units contain only one kind of atom. The point I wish to emphasize is that the conditions which determine the formation of these metallic compounds are of quite a different kind from those which determine the formation of gaseous compounds containing one or more electronegative constituents. With these it is the valency conditions, such as may be expressed by the formation of octets, which govern the type of admissible compound; with the metals, on the other hand, the formation or not of a compound is determined by the potential energy possessed by a unit of the lattice system formed by the compound. As this potential energy depends on the number of electrons as well as upon the number of atoms in the unit, and as the number of electrons depends upon the valencies of the atoms, valency will have an influence upon the type of compound, but of a different character to that exerted in compounds between metals and electronegative elements. From these considerations we should expect that the structure of intermetallic compounds would not conform to the condition of valency as ordinarily understood. We find, for example, many stable compounds in which two atoms of a bivalent metal are combined with one atom of a univalent one, *e.g.*, $NaCd_2$, KHg_2, $CuMg_2$, a proportion inconsistent with the usual conception of valency, but one which would be satisfied by a very simple form of unit cell. Thus if the divalent atoms were at the corners of a hexagonal prism and the monovalent atom at the centre, while the electrons were placed at the centres of side faces of the prism and two along the axis on either side of the monovalent atom, we have a unit containing two divalent atoms, one monovalent atom and five electrons.

MIXED CRYSTALS AND INTERMETALLIC COMPOUNDS.

Metallurgists distinguish between two types of combination between metals. The one type called intermetallic compounds consists of alloys of a composition at which on a graph representing the relation between percentage composition and some physical property, such as electrical conductivity, shows a well-marked maximum or minimum. These points in general correspond to alloys in which the proposition between the numbers of atoms of the two metals are expressed by simple ratios. Alloys of other composition represented by the regions between the maxima and minima are supposed to be in a state which is sometimes described as mixed crystals and sometimes as solid solutions.

Let us consider the question of the combination of two metals A and B from the point of view of the electron theory of solids. There are several possibilities, the alloy might be a mechanical mixture of A and B; by this we mean that the atoms of A and B are respectively arranged in their own space lattices, and that there are no composite space lattices made up of atoms of A and B arranged in regular sequence. Another alternative is that the atoms should be arranged in composite space lattices, the atoms along the lines of the lattices consisting partly of A atoms and partly of B. Here there are again several possibilities, for with a fixed proportion between the number of A atoms and the number of B there are many different composite lattices possible. Thus, for example, if there are three A atoms for one of B, we might in two dimensional lattices have the spacings

I.

a a a a a a a a a
a b a b a b a b a
a a a a a a a a a
a b a b a b a b a

or

II.

a a a b a a a b a a a b a a a
a b a a a b a a a b a a a b a
a a a b a a a b a a a b a a a

or

III.

a a b a a b a a b a a b a a b
a a a a a b a a a a a b a a a
a a b a a b a a b a a b a a b

Thus the alloy might consist either of one kind of lattice or a mechanical mixture of a number of different kinds. If the atoms have been in a condition in which they could diffuse freely, *e.g.*, if the alloy were stirred for a long time when the melt was liquid, the arrangement would be that corresponding to minimum potential energy, remembering that when there is a mechanical mixture of different phases we must take into account the energy due to surface tension. When there is a well-marked minimum in the potential energy for one arrangement of the atoms, we should expect that the alloy would be homogeneous and represented by a single lattice corresponding to this arrangement. If, on the other hand, there are several arrangements which differ but little from each other in potential energy we might expect to find all these arrangements present in the alloy in proportions which would vary with the temperature. When the alloy is homogeneous and the arrangement of atoms and electrons capable of being represented by a single lattice, it corresponds on my view to an intermetallic compound. When, however, there are several different arrangements mixed together, it corresponds to a solid solution.

When the atoms of A and B carry the same charge of electricity, then if A is greatly in excess we should expect the B

atoms to occupy positions along a space lattice that differed but little from that for pure *A*. When, however, the number of the *B* atoms increase beyond a certain proportion, there will probably be large modifications in the space lattice for the mixture and possibly the formation of one of quite a different character. The probability of a new type of space lattice will be much increased if *B* and *A* carry different electrical charges, *i.e.*, have different valencies.

Let us consider from this point of view the changes we might expect in the properties of a mixture of two metals, *A, B,* starting from pure *A* and ending with pure *B*.

When *A* is greatly in excess, the formation of those compounds which contain a comparatively large proportion of *A* in comparison with *B* will, in accordance with the principles of mass action, be promoted, and the mixture will consist of free *A,* little or no free *B,* and a number of compounds, the majority of which contain an excess of *A* over *B*. As the proportion of *B* increases the amount of free *A* diminishes and the proportion between the amounts of different types of compounds changes, the change being mainly at the expense of those which contain a large number of *A* atoms. When the mixture is such that the proportion between *A* and *B* is that of a possible compound, if that compound is one which has markedly less potential energy than its constituents, the whole mass of metal at low temperatures at any rate may practically consist of this compound. It need not, however, do so in all cases; there may be a certain amount of dissociation of the compound depending upon the temperature. Again, if there is another compound with very small potential energy, some of it is pretty sure to be formed, so that the mixture may not be quite homogeneous even when the proportions are those of a possible compound. When the mixture consists almost entirely of one compound, its constitution is identical in many respects with that of a simple metal. All the units of which it is built up are of one kind, and that kind an arrangement of atoms and electrons, which when the units are united give, as in the cases of metals, a system of lattices for atoms and electrons. Any general property possessed by all metals would, we should expect, be possessed by this compound. In particular the conduction of electricity through the compound would take place by the same mechanism as through metals. Now one peculiarity of the conduction of electricity through pure metals is that the temperature coefficient of the electrical resistance is much the same for all metals, hence we should expect that the temperature coefficient of an intermetallic compound would be about that of the pure metals. There seems to be very considerable evidence[36] that this is approximately true.

The temperature coefficient of the electrical resistance when the mixture of the two metals contains several compounds is often very much smaller than that for pure metals; in fact, it is even sometimes of opposite sign. When there are several different components the effect of a rise in temperature will be an increase in the dissociation and hence an alteration in the proportion of the amount of different compounds present in the alloy. The more complicated compounds will be split up by the rise in temperature and the proportion of simpler ones increased. As the lattices formed by the complex compounds are more intricate than those of the simpler ones, we should expect their electrical resistance to be greater so that when some of these are split up owing to the rise in temperature there will be a tendency to reduce the resistance. Thus in a mixture of this kind there is, in addition to the normal effect which makes the resistance increase, an effect tending to make the resistance fall when the temperature rises; this will diminish the temperature coefficient of the resistance.

Let us now consider the changes in the elastic properties produced by the formation of these intermetallic compounds. We have seen that in the solid state the potential energy of an atom and its associated electrons is equal to

$$-4\cdot5\,\frac{k_A}{N_A} \tag{92}$$

when k_A is the bulk modulus and N_A the number of atoms in unit volume for the element A. Since $N_A = \triangle_A / M_A$ where $\triangle_A$ is the density of A and M_A the mass of its atom, the potential energy per atom may be written as

$$-4\cdot5\,k_A\,\frac{M_A}{\triangle_A} \tag{93}$$

Thus the potential energy of n atoms of a metal A and m of a metal B before they combine is equal to

$$-4\cdot5\left(k_A\,\frac{nM_A}{\triangle_A}+k_B\,\frac{mM_B}{\triangle_B}\right) \tag{94}$$

---

[36] "Desch. Intermetallic Compounds," p. 52.

If these unite to form the compound A_nB_m, the potential energy per molecule of this compound is

$$-\,4{\cdot}5\,\frac{k_{nm}}{\Delta_{nm}}\,(nM_A + mM_B) \qquad (95)$$

Where k_{nm} is the bulk modulus of the compound and Δ_{nm} its density. Thus by the formation of the compound, the diminution of potential energy per molecule of the compound formed is

$$4{\cdot}5\left\{\frac{k_{mn}}{\Delta_{mn}}\,(nM_A + nM_B) - \left(\frac{nk_AM_A}{\Delta_A} + \frac{mk_BM_B}{\Delta_B}\right)\right\} \qquad (96)$$

and this must be equal to the heat of formation per molecule of the compound at zero absolute temperature. Thus from the compressibilities of the compound and those of its constituents we can calculate the heat of formation of the compound.

Again

$$\frac{nk_AM_A}{\Delta_A} + m\,\frac{k_BM_B}{\Delta_B} = K\left(\frac{nM_A}{\Delta_A} + \frac{mM_B}{\Delta_B}\right) \qquad (97)$$

and

$$\frac{nM_A}{\Delta_A} + \frac{mM_B}{\Delta_B} = \frac{nM_A + mM_B}{\Delta} \qquad (98)$$

Where K is the bulk modulus and Δ the density of the mixture, calculated on the assumption that A and B exert no influence on each other, hence the diminution in potential energy due to the formation of the compound may be written in the form

$$4{\cdot}5\,(nM_A + mM_B)\left\{\frac{k_{mn}}{\Delta_{mn}} - \frac{K}{\Delta}\right\} \qquad (99)$$

Now the compound will not be formed unless the potential energy diminishes. Hence $\frac{k_{mn}}{\Delta_{mn}} - \frac{K}{\Delta}$ must be positive, or if, as is generally the case, Δ_{mn} is very nearly equal to Δ, k_{mn} must be greater than K; in other words, the compound must be less compressible than a mechanical mixture of the metals. It is a general rule that the " hardness " of an alloy is greater than we should expect from its composition, and though hardness is not the same thing as the reciprocal of the compressibility yet some of the tests used to measure the hardness, *e.g.*, the indentation produced by a loaded ball, seem almost more a test of compressibility, the result that combination diminishes the compressibility seems to be indicated.

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